Brandenburg University of Technology Cottbus
Faculty of Environmental Sciences and Process Engineering
International Course of Study: Environmental and Resource Management (PhD)

DOUBLE STAGE DRY-WET FERMENTATION OF UNSORTED MUNICIPAL SOLID WASTE

By

Fei-Baffoe Bernard

Submitted in accordance with the requirements for the degree of

PhD

Faculty of Environmental Sciences and Process Engineering

Department of Waste Management

Examination Committee:

Chairman: Prof.Dr.-Ing.Wolfgang Spyra
Examiner: Prof. Dr.-Ing. Günter Busch
Examiner: Prof. Dr.-Ing. Peter Ay

Date of oral defence: July 17, 2006

Cottbus 2006

Brandenburgische Technische Universität Cottbus
Fakultät für Umweltwissenschaften und Verfahrenstechnik

Internationaler Studiengang für Umwelt- und Ressourcen-Management (PhD)

ZWEISTUFIGE TROCKEN-NASS-FERMENTIERUNG VON UNSORTIERTEN SIEDLUNGSABFÄLLEN

von

Fei-Baffoe Bernard

Eingereicht gemäß den Anforderungen zur Erlangung des akademischen Grades eines

PhD

Fakultät für Umweltwissenschaften und Verfahrenstechnik

Abteilung Abfallwirtschaft

Promotionsausschuß:

Vorsitzender: Prof.Dr.-Ing. Wolfgang Spyra

Berichter: Prof. Dr.-Ing. Günter Busch

Berichter: Prof. Dr.-Ing. Ay

Tag der wissenschaftlichen Aussprache: 17. Juli 2006

Cottbus 2006

DECLARATION

I declare that the work submitted is my own and that appropriate credit has been given where reference has been made to the work of others.
This dissertation has never been presented for a degree in this or any other university, neither published at national or international level.

Signed by Supervisors:

Prof. Dr.-Ing. Günter Busch .....
Chair of Waste Management, BTU Cottbus

Prof. Dr.-Ing. Peter Ay ……
Chair of Mineral Processing, BTU Cottbus

Signed by PhD Student:

Fei-Baffoe Bernard (M.Sc.) ……
Chair of Waste Management, BTU Cottbus

ACKNOWLEDGEMENTS

I wish to express my deepest appreciation to Prof. Günter Busch my supervisor for his invaluable comments and excellent supervision. I must also thank him for the cordial relations showed towards me, which was very helpful and very much cherished.

My thanks go to Prof. Peter Ay for accepting to be my second supervisor and his assistance.

I also extend my appreciation to Mr. Marko Sieber for all his effort in assisting me with waste for my experiments and the technical support rendered to me.

Further, I wish to thank Mrs Regine Nickel and Mr. Ulrich Klopsch for their assistance in the laboratory. My thanks also go to the entire members of the department for their support in one way or the other in realising this dissertation.

My hearty thanks to Benedicta my wife for her encouragement and moral support.

My sincere thanks also go to the following persons Rajeev Kavety, Daniel Nukpezah, Alfred Osei, Andrew De-Heer, Nana Kwabena Osei, and McDaniel Yeboah Nortey, for their diverse assistance in the preparation of this dissertation.

I am also grateful to my in-laws Mr and Mrs Amoah for their prayer and support as well as all members of my family.

I wish to thank Mr and Mrs Schirmer for their wonderful support during my stay in Germany and the realisation of this thesis. My thanks also go to Mrs Michalczyk, Miss Ingrid Rotter, Aniela Lichy and Pfr.Dr. Thomas Olickal for their support and prayer.

My special thanks go to my uncle Mr Opia Mensah Kumah and Okyere Baffour Akwasi for their encouragement and support towards my academic career.

Finally I thank the most high God for the strength and the calm through the perplexing times during my study.

DEDICATION

This work is dedicated to God Almighty and to all whose sacrifice and prayers have brought me this far.

ABSTRACT

Aim of the study

In this thesis, the recovery of biogas from Unsorted Municipal Solid Waste with high methane content was investigated. Special attention was given to unsorted municipal solid waste since its management is posing a big challenge for solid waste management authorities especially in developing countries (e.g. Accra, Ghana). Common solid waste management practice in most of the communities involves having the entire components of the waste mixed together and deposited in bins or on a bare ground at locations within communities and subsequently hauled to the dumpsite by the waste authority. In a laboratory study, a simulated waste was developed representing the real waste situation in Accra, Ghana to leach out the biodegradable organic fraction and subsequent biogas recovery.

Method of investigation

In order to optimize the biodegradation of Unsorted Municipal Solid Waste, the double-stage anaerobic digester with optimum design capability and with both intra and inter liquid recirculation, and microaerophilic hydrolysis conditions was employed.

In order to biomethanize the waste, the following hypotheses were tested:

- Effect of water flow rate (dilutions) on the extent of hydrolysis/ liquefaction.
- Solid retention time and biodegradation.
- Temperature on the extent of hydrolysis.
- Effect of preprocessed feeding material on hydrolysis and gas yield.

Results and technical applicability

The results indicate that the various conditions tested are effective in determining the biogas production from the Unsorted Municipal Solid Waste. Following several runs for the optimization process, volume and mass reduction of 30±19% and 42±13% was achieved respectively. Importantly, almost 42% of the organic total solids reduction with equivalent of methane yield of 232±66 l CH_4/kg OTS was obtained. A concept is developed for the application of the double-stage digester for the biomethanization of Unsorted Municipal Solid Waste. This concept involves the appropriate optimum conditions required for the biodegradation process. Finally the potential of using Unsorted Municipal Solid Waste for commercial biogas production was emphasized.

KURZFASSUNG

Ziel der Studie

In dieser Doktorarbeit wurde die Gewinnung von Biogas aus unsortierten Siedlungsabfällen mit einem hohen Methangehalt untersucht. Besondere Aufmerksamkeit wurde den unsortierten Siedlungsabfällen gewidmet, da deren Entsorgung eine große Herausforderung für die Abfallentsorgungsunternehmen, insbesondere in den Entwicklungsländern (z.B. Accra, Ghana), darstellt. In den meisten Kommunen ist es bei der Feststoffabfallentsorgung üblich, dass alle Abfallkomponenten vermischt werden und in Abfallbehältern oder auf dem Boden an Standorten in den Kommunen gelagert werden, bis sie schließlich von den Entsorgungsunternehmen zur Deponie transportiert werden. In einer Laborstudie wurde ein simulierter Abfall entwickelt, der die reale Abfallsituation in Accra, Ghana, zur Auswaschung des biologisch abbaubaren organischen Anteils und der anschließenden Biogasgewinnung darstellt.

Untersuchungsmethode

Um den biologischen Abbau der unsortierten Siedlungsabfälle zu optimieren, wurde der zweistufige sauerstoffunabhängige Faulbehälter (Digestor) mit optimal ausgelegter Leistung und mit einer Rezirkulation der Flüssigkeit sowohl intern als auch extern eingesetzt und es wurden Hydrolyse-Bedingungen angewendet, bei denen wenig Sauerstoff benötigt wird (micro-aerophilic).

Für eine Biomethanisierung des Abfalls wurden folgende Hypothesen getestet:

- Auswirkung der Wasserdurchflussrate (Verwässerungseffekte) auf die Menge der Hydrolyse/Liquefaction
- Verweilzeit der Feststoffe und biologischer Abbau
- Temperatur auf den Umfang der Hydrolyse
- Auswirkung des vorbehandelten zugeführten Materials auf die Hydrolyse und den Gasertrag

Ergebnisse und technische Anwendung

Die Ergebnisse zeigen, dass die verschiedenen getesteten Bedingungen effektiv bei der Untersuchung der Biogasproduktion aus unsortierten Siedlungsabfällen sind. Nach verschiedenen Durchläufen für den Optimierungsprozess wurde jeweils eine Volumen-und Massenreduzierung von 30±19% und 42±13% erreicht. Wichtig ist, dass fast 42% der Reduzierung der gesamten organischen Feststoffe mit dem

Äquivalent der Methanausbeute von 232±66 l CH_4/kg OTS erhalten wurde. Es wurde ein Konzept zur Anwendung des zweistufigen Faulbehälters für die Biomethanisierung von unsortierten Siedlungsabfällen entwickelt. Dieses Konzept beinhaltet die entsprechenden optimalen Bedingungen, die für den biologischen Abbauprozess erforderlich sind. Am Ende wurde die Möglichkeit der Verwendung unsortierter Siedlungsabfälle zur kommerziellen Biogasproduktion hervorgehoben.

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LIST OF ABBREVIATIONS

AD	Anaerobic Digestion
AMA	Accra Metropolitan Assembly
BOD	Biological Oxygen Demand
BTA	Biotechnische Abfallverwertung GMbh & Co
CH_4	Methane
CLD	Causal Loop Diagrams
CO_2	Carbon dioxide
COD	Chemical Oxygen Demand
CSTR	Continuously Stirred Tank Reactors
EU	European Union
EGSB	Expanded Granular Sludge Bed
GNA	Ghana News Agency
H_2	Hydrogen
HCl	Hydrogen Chloride
H_R	Hydrolysis Reactor
HRT	Hydraulic Retention Time
H_2S	Hydrogen Sulphide
IFPRI	International Food Policy Research Institute
ISWM	Integrated Solid Waste Management
JICA	Japan International Cooperation Agency
kWh	Kilo Watt Hour
LOI	Loss On Ignition
M_R	Methane Reactor
NH_3	Ammonia
OA	Organic Acid
OFMSW	Organic Fraction of Municipal Solid Waste
OTS	Organic Total Solids
OLR	Organic Loading Rate

PVC	PolyVinyl Chloride
RCRA	Resources Conservation and Recovery Act
SMP	Specific Methane Production
SRT	Solid Retention Times
TC	Total Carbon
TIC	Total Inorganic Carbon
TKN	Total Kjeldahl Nitrogen
TOC	Total Organic Carbon
TON	Total Organic Nitrogen
TS	Total solids
UASB	Upflow Anaerobic Sludge Blanket
UNEP	United Nations Environment Programme
UMSW	Unsorted Municipal Solid Waste
US	United States
VFA	Volatile Fatty Acids
VS	Volatile Solid
WMD	Waste Management Department
MSW	Municipal Solid Waste

1 INTRODUCTION

1.1 Background

The quest for a systematic management of an ever increasing trend of Municipal Solid Waste (MSW) generation coupled with the complex waste characteristics is a big challenge for solid waste management in both developed and developing countries. The unprecedented rate of urbanization and industrialization all over the world has created a lot of problems in respect to solid waste management especially in major cities of African countries. Resident populations have increased in numbers and public facilities have not kept pace with the increased amounts of urban wastes (Sheehan et al., 2006). Consequently, accumulation of large volumes of solid waste in public places has become common scenes in these cities. These have immediate public health implications, which are manifested as frequent outbreak of major epidemic diseases (cholera and diarrhea), increased flood rates and high risk to public health (Ajeam-Ragee, 2002 and Fobil et al., 2002).

One of the main arguments for justifying the situation in developing countries is the high cost of sanitation facilities provision and the lack of capital resource to invest in the sector. Long-term and reliable final disposal system is also another area posing a major environmental challenge particularly in developing countries. In order to solve this problem, many experts in the field of waste management have studied various waste management techniques and control strategies. However, the need and demand to manage large volumes of waste through landfilling as the final disposal option still remains a dilemma.

The various technological possibilities for the treatment of municipal solid waste known today include landfilling, incineration, aerobic stabilization (composting) and anaerobic digestion (AD). Generally, landfilling is known to be the most economical and dependable MSW disposal system being practiced worldwide. It plays an indispensable role in integrated solid waste management schemes. Based on the fact that all waste processing methods generates residues that cannot be further reused or recovered, must eventually be landfilled (Plaza et al., 1996). Historically, landfilling of municipal solid waste (MSW) was the usual main disposal route and was not given an early critical emphasis on its stability and behaviour even though it was known to create detrimental environmental consequences that could affect the health and lives of all living creatures. Despite the negative impact of direct landfilling, it can not be neglected that large volumes of untreated MSW stream are subject to landfilling at present, especially in the developing world.

Generally, the MSW composition in Africa represents a large fraction of waste that is highly biodegradable in nature. Importantly, it has been realized that the organic portion of waste in the landfill causes harmful pollutants that accumulate and affect the state of the environment. Thus by reduction of the organic fraction of MSW stream, it is possible to reduce landfill emissions and also to recover valuable by-products like biogas for energy conversion. Also, the remaining stabilized material after treatment can be used as soil conditioner or landfilled. In this respect, pretreatment of municipal solid waste by biological process prior to landfilling can be viewed as an integral part of the solid waste management scheme. This concern serves as an allowable scope of action towards the recognition of a sustainable pretreatment technology before landfilling, i.e., the anaerobic digestion.

The process of anaerobic digestion is a biological process which makes use of anaerobic bacteria to break down organic waste, converting it into a stable solid and biogas, which is a mixture of carbon dioxide and methane. The anaerobic digestion process is very attractive because it yields biogas which can be used as renewable energy resources and also produce reduced stabilized material after treatment (Polprasert, 1996 and Wang et al., 2002).

Based on the advantages, anaerobic digestion of solid waste is rapidly gaining strength to new advances especially the fermentation of both sorted and unsorted Municipal solid waste (Stenstrom et al., 1983). Anaerobic digestion appears to be the most reliable and promising process for the treatment of organic solid waste (Palmowski et al., 2003 and Christ et al., 1999). Compared to other conversion technologies for organic fraction of MSW, the economy, energy, and the environmental advantages makes the process an attractive treatment option (Stenstrom et al., 1983 and Ostrem, 2004). Notably, several research studies have been done in the field of anaerobic digestion of solid waste, yet the application of this process is not widely practised especially in developing countries due to the lack of appropriate treatment systems for the type and characteristics of MSW present. In addition, complexities of the solid waste in most developing countries do not promote sorting of waste at source, which implies that the waste has to be treated in its unsorted form to stabilize it first, after which sorting can be done or landfilled. Therefore, there is a need for the development of a high-rate anaerobic digestion technology that has the full capability to treat unsorted municipal solid waste.

Thus, this study is designed to carry out a controlled high-rate biomethanization of Unsorted Municipal Solid Waste by the double-stage dry-wet digestion as pretreatment option prior to landfill.

1.2 Objective of the research

The overall objective of the research is to generate biogas from unsorted municipal solid waste (UMSW) and as well as significantly reduce the mass and volume of organic matter to minimize environmental pollution caused by landfills (dumping sites).

The specific assignments/objectives carried out in order to achieve the overall objective of the research were:

- First hand overview of the solid waste management situation in Accra, Ghana.
- Reviewing of literature for the basics on fermentation process of municipal solid waste.
- Evaluation of the influence of various water flow regimes introduced into the hydrolysis reactor and their resulting performance on Organic Acid (OA) and Chemical Oxygen Demand (COD) production, pH and overall waste degradation.
- To determine the shortest solid retention time in the hydrolysis stage of the conversion of the waste.
- To determine the influence of temperature on the hydrolytic and acidogenic conversion of UMSW.
- To verify the importance of source sorted, mechanically sorted (8-40mm, 40-120mm) and shredded wastes effect on particulate matter hydrolysis and their corresponding biogas yield.
- Evaluation of the double stage digestion as viable technique for the pre-treatment of UMSW.

1.3 Rationale for the research

The rapid increase and accumulation of solid waste in major cities of low income countries (e.g. Accra, Ghana) and its associated risk to human health is a source of principal concern. The waste composition is characterized by high fraction of biodegradable organic material that is potentially recyclable for energy production. Currently, there are no recycling programmes in place to exploit this organic fraction but instead hauled into a dumpsite and wasted, resulting in negative impacts on both human health and the environment. Uncontrolled anaerobic digestion takes place releasing leachate into groundwater and emission of potential greenhouse gases such as methane and carbon dioxide into the atmosphere. Besides, disease causing bacteria and foul odour are also released from the decomposing materials into the environment resulting in increased cases of cholera, diarrhoea, intestinal worms and upper respiratory diseases.

Common solid waste management practice in most of the communities involves having the entire components of the waste mixed together and deposited in bins or on a bare ground at locations

within communities and subsequently hauled to the dumpsite by the waste authority. Sorting of waste at source is not done and cannot be achieved in the interim based on many factors which includes socio-economic and cultural behaviour of the people. It is therefore imperative to find an appropriate pretreatment option for unsorted municipal solid waste.

Landfilling the solid waste without any pretreatment will constitute a very huge environmental consequence both now and in the near future as it has been pointed out earlier. In addition, landfill or dumpsite spaces are decreasing at a fast rate and there is difficulty in finding suitable locations and also getting public approval. Huge investment costs are involved in well engineered sanitary landfill facilities. It is therefore essential to look for and implement long-term integrated waste management strategies that ensure a sustainable approach for waste management services.

Among the preferred pretreatment options are composting and anaerobic digestion. With regards to composting, to obtain high quality compost which is a desired objective for the process would require an uncontaminated feedstock, i.e., highly sorted organic fraction which cannot be achieved based on existing solid waste management practices. This implies that pretreatment plants for the unsorted municipal solid waste (UMSW) have to be equipped with several pretreatment steps to remove foreign materials, to sanitize hygienic risky wastes and to upgrade the waste for digestion. Inclusion of sorting facilities would involve some level of cost and labor, and looking at the putrescible nature of the waste and the extent of decomposition under the tropical conditions, excessive handling by personnel would constitute serious health problems from a sanitary perspective. In addition, complicated sorting plant involving the use of screens, pulpers, drums, presses, breakers and flotation units would inevitably result in a loss of volatile solids (Lissen et al., 2001). However, in the case of anaerobic digestion, unsorted municipal solid waste could be used directly even though sorted waste would have been preferred. Anaerobic digestion would yield biogas and reduce the mass and the volume of the solid waste substantially after digestion. The digested waste or digestate is stabilized and can be sorted out after being dried or landfilled with little environmental consequence. When practiced it can provide a wide range of advantages in addition to the renewable energy (biogas). These include waste treatment, pollution reduction, odours and disease reduction and recycling of nutrients back into the soil.

2 PROBLEM ANALYSIS AND COMMON PRACTICES IN WASTE MANAGEMENT

2.1 Municipal Solid Waste situation in developing countries

2.1.1 Introduction

At present the acceptable method of disposal of solid waste in most developing countries especially in Africa is that of direct burial or burning at landfills (JICA, 1999). While in advanced countries efforts are being made through strict directives to fully engage in processes that will avoid landfilling, developing countries are still struggling to have sanitary landfills and hence abolishing landfills is not of immediate concern.

Changes in waste management policies in recent times especially in advanced countries have shifted waste management planning from reliance on landfill towards integrated solid waste management (ISWM) approaches. For example, new directives/legislations are being promulgated in the EU and the US on waste disposal in the interest of the environment. In 1993, the United States' Resources Conservation and Recovery Act (RCRA) subtitle D requires that landfills must be impermeably lined and equipped with leachate and gas collection equipment (Anomanyo, 2004). In the European Union (EU), policy on waste management was expressed in the Fifth Environment Action Programme 'Towards Sustainability' [COM (92)23] issued in March 1992, sets long-term policy objectives and intermediate targets for the year 2000. For 'Municipal solid waste,' the overall target is the 'rational and sustainable use of resources' to be achieved through a hierarchy of management options, such as prevention of waste, recycling and re-use, safe disposal of remaining waste in the following rank order: Combustion; Incineration and Landfill. Thus, it is clear that the European Union views landfill as the final waste disposal option and which has been translated into potentially increasing stringent controls over landfill of waste [COM (93)275] (Hester et al., 1995).

In Germany for example, the implementation of the landfill Directive prescribes that from June 2005 only thermally or mechanically-biologically pretreated MSW can be landfilled (Lechner, 2005). The goal of the German government is to reduce the disposal of organic wastes and to promote their recycling and utilization as a renewable energy source. Therefore, the *Recycling and Treatment of Wastes Act* (Kreislaufwirtschafts – und Abfallgesetz 1994) combined with the *Technical Instructions on Urban Wastes* (TA-Seidlungsabfall 1993) and the *Biowaste Ordinance* (Bioabfallverordnung 1998) was established. This has increased the relevance of anaerobic organic waste treatment technologies as one of the most beneficial technologies for wet wastes.

Additionally, the production of biogas as a renewable energy source is strongly supported by the government in order to decrease the CO_2-emissions according to the Kyoto protocol (Weiland, 2000).

Generally, these policies and their enforcement have helped the developed nations in implementing the waste hierarchy; prevention, materials recovery, incineration and landfill (Ostrem, 2004). In the developing world however, poor enforcement or non-existence of waste management policies have resulted in the dependence on open dumping. Improvements in the area of constructing sanitary landfills in these regions have most often supported by the World Bank and other bilateral donor agencies. The troubling part of the landfill situation in most developing countries is that, they are just dumpsites and not engineered so wastes are dumped any how which limits their capacity. Therefore, these dumpsites will not be able to accommodate increased amounts of garbage because of these limitations. To continue to use landfills means the opening of more landfills and this may not be a viable solution because of scarcity of land space and environmental concerns.

Organic waste is also responsible for pollution of soil and water bodies through leachate, and in the process of uncontrolled anaerobic digestion it contributes to global warming from the methane produced (Ahmed and Zurbrugg, 2002). A possible step in mitigating these effects is enhancing resource-recovery activities of the organic waste fraction. An obvious treatment and recovery option for organic waste is the biological, treatment option for that matter AD.

With respect to the criteria of sustainable waste management, the controlled AD of putrescible wastes has several advantages (Polprasert, 1996). It is faster than AD taking place in common landfills. It yields usable energy whereas combustion and composting require a net energy input. Organic materials and nutrients may be recycled whereas combustion destroys both organic material and some nutrients. Anaerobic digestion is the only process, which achieves both energy utilization and stabilization.

The approach of pretreating waste before landfilling is a laudable idea. As the complexicity and heterogeneous nature of solid waste calls for a different waste management options, it must be put together as a unit to effectively handle all the different materials in the waste stream. This approach falls within the philosophy of integrated solid waste management (ISWM)(Fobil et al., 2002), which states that management subsystems such as source reduction, reuse, recycling, recovery, incineration, treatment and landfilling, must function in tandem with each other and should not be seen as hierarchical order of superiority (Keith, 1994).

2.1.2 Integrated solid waste management

According to Tchobanoglous et al. (1993), integrated solid waste management is defined as the selection and application of appropriate techniques, technologies, and management programs to achieve specific waste management objectives and goals. Understanding the interrelationships among various waste activities makes it possible to create an ISWM plan where individual components complement one another. Figure 2.1 shows the synergistic nature of integrated solid waste management.

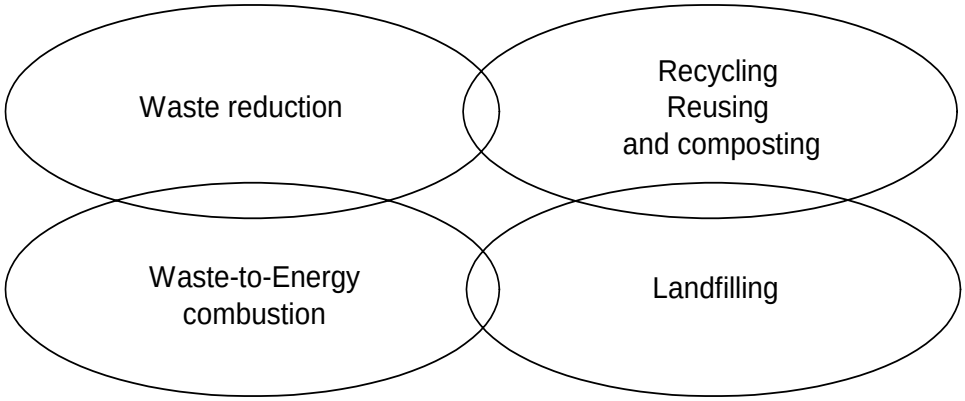


Figure 2.1. Synergism of integrated solid waste management (Keith, 1994).

Within the philosophy of ISWM, systems are interrelated and are selected to complement each other. Some problems can be solved more easily in combination with other aspects of the waste system than individually. For example, the separate collection of yard wastes can be used to effect positively the operation of waste-to-energy combustion facility (Tchobanoglous et al., 1993).

The United Nations Environment Programme (UNEP) international Environmental Technology Centre (1996) acknowledges the importance of viewing solid waste management from an integrated approach:

- Adjustments to one area of the waste system can disrupt existing practices in another area, unless the changes are made in a coordinated manner.
- Integration allows for capacity or resources to be completely used; economies of scale for equipment or management infrastructure can often only be achieved when all of the waste in a region is managed as part of a single system.
- Public, private, and informal sectors can be included in the waste management plan.
- An ISWM plan helps identify and select low cost alternatives.

Some waste activities separately cannot handle any charges; some will always be net expenses, while others may show a profit. Without an ISWM plan, some revenue- generating activities are "skimmed off" and treated as profitable, while activities related to maintenance of public health and safety do not receive adequate funding and managed insufficiently.

The general waste hierarchy accepted by industrialized countries is comprised of the following order: reuse, recycling, recovery, treatment and landfilling. The objective of source reduction is reducing the amount of waste that is generated in the initial place. This can be achieved through the design, manufacture, packaging of products with minimum volume of material, or a longer useful life. Reusing the generated waste material instead of throwing it away or wasting is the preferred option. Recycling involves converting of the unwanted material into useful products and this will help reduce the demand on resources and the amount of waste requiring disposal by landfilling. With current advancement in technology, the recycling of waste creates a wide option in waste management. Despite the amount recycled there would always be remaining waste residues that cannot be recycled, and for that matter needs to be incinerated.

Despite progress in a few countries, fundamental environmental, financial, institutional and social problems still exist within all components of waste systems in developing countries, e.g: Ghana. Common to all countries is an increasing awareness about the linkages between waste generation and resource consumption vis-à-vis sustainable development; greater involvement of the business community in recycling; and the increasing awareness of the value of source separation and marketability of good quality compost. Incineration is mainly used for volume reduction and its high costs will continue to inhibit its use especially in developing countries. Finding sites for landfills is difficult, which often causes sites to be established in inappropriate locations. In addition, increasing attention is focused on reducing greenhouse gas emissions from waste.

2.1.3 Conceptual framework and theoretical background of solid waste management

"The world will not evolve beyond its present state of crisis by using the same thinking that created the situation"

- Albert Einstein

This research is based on the concept development of an integrated waste management system that has the ability to include economic, environmental and social compatibilities as the aspects of a sustainable waste management system. This focuses on the existing waste management system, the feasibility of anaerobic pretreatment of the unsorted municipal solid waste and the integration of the waste management practices.

In order to develop a sound waste management concept, there is a need for system thinking which emphasizes problem solving (Hall et al., 2004). System thinking helps in viewing the entire waste management concept from a broader perspective through structures, patterns, events and feedback as compared to just an event (Anderson et al., 1997). Thus via system thinking a comprehensive understanding is achieved from systems or factors that initially were apparently remote (Haines, 2000).

In practical application, system analysis (system thinking process) is employed and causal Loop Diagrams (CLDs) are used to reflect the interactions of the various systems (Groff et al., 2003; Sherwood, 2002 and Gaynor, 1998).

The causal loop diagram which can be considered as a system is a group of interacting, interrelated, or interdependent parts that form a complex and unified whole that has a specific purpose (Anderson et al., 1997 and Kim, 1999).

In this research, system thinking is applied in its practical form thus system analysis employs the use of casual loop diagrams. Here much focus is placed on the existing waste management system, the feasibility of anaerobic pretreatment of the unsorted municipal solid waste and the integration of the waste management practices.

The system analysis is utilized to comprehend the existing waste management system and the potential of anaerobic waste treatment as an integral part of the sustainable waste management. It aided in describing the interactions through cause and effects (causalities) between variable systems and their active circular influence and the extent to which these systems are interconnected.

In the next section, a detailed analysis of the solid waste management practices and problems in the Accra metropolis, the capital and the administrative city of Ghana is presented. Most of the problems highlighted are centred on the environmental and social aspect. In addition, a basis is provided for why anaerobic waste pre-treatment is urgently needed in the waste management hierarchy to combat the waste disposal problems in the city.

2.2 Situation review: Solid waste management in Accra-Ghana

2.2.1 Solid waste management in Accra

The Waste Management Department (WMD) of the Accra Metropolitan Assembly (AMA) is responsible for garbage collection, disposal, and general sanitation within Accra.

Presently, problems are encountered at all levels of the waste management hierarchy of the metropolis – from collection, transportation to final disposal of the solid waste. While existing

solid waste disposal facilities are inadequate to deal with the quality and quantity of waste generated, pre-treatment systems before landfilling are currently not in use.

In order to effectively comprehend the facets of the existing waste management in Accra, a system analysis concept making use of Causal Loop Diagrams (CLDs) which illustrate the interactions of the various systems and the possibility of integrating anaerobic treatment of waste is employed. In the CLD language, a '+' sign at the head of the arrow indicates a positive relationship between the two connecting variables at the arrowhead and the tail.

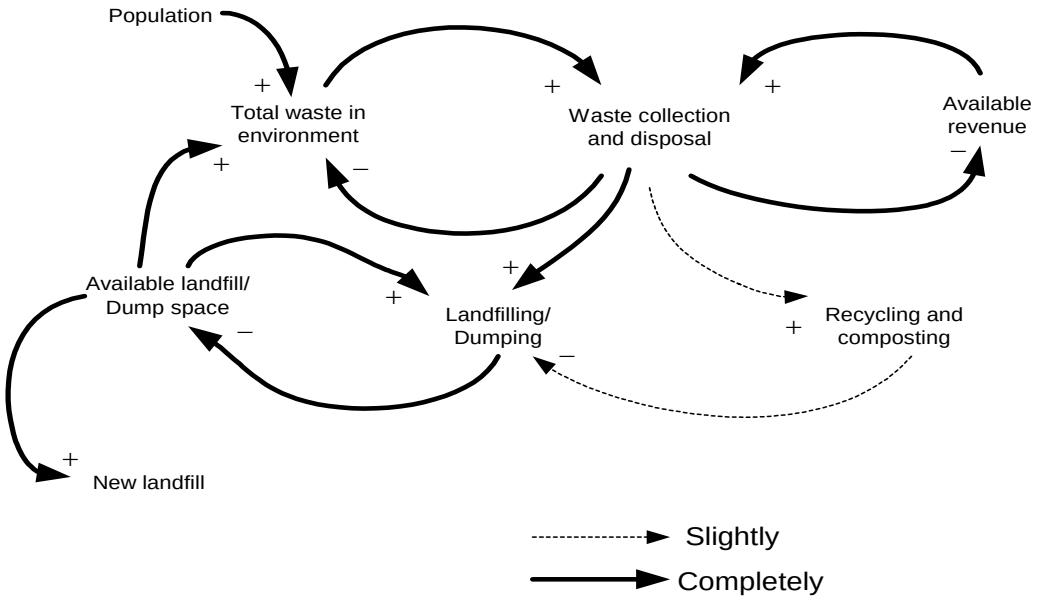


Figure 2.2. Causal Loop model for existing waste management system

Causal Loop diagram for existing waste management system is represented in figure 2.2 starting from the top left of the loop, resources are used in production and the products are utilized by the population generating waste in the environment. The amount of waste collected and disposed of determines the waste in the environment. Considering the top right loop, collection and disposal processes depend on the available revenue for the supply of collection and disposal equipment. The loop at the bottom indicates that most of the solid waste collected and disposed off from the metropolis ends up in the landfill or dump site with very little recycling or composting. A decrease in landfill or dump space has occurred as a result of increased landfilling and dumping and subsequently has also lead to a decrease in amount of waste collected and dumped. This has resulted in a flow-back of waste into the environment and therefore there is a need for the construction of a new landfill.

The waste management department of the AMA makes no provision for income generation from its activities. It receives its funding, on one hand from internally-generated funds which is very

small and on the other, from the Common Fund of the government. Evidently, this is not sufficient as the major generators of waste do not pay for collection (Chronicle, 2004). There is the need therefore to introduce waste treatment (anaerobic digestion) and management systems that will optimize land-use, reduce emissions to the environment and generate revenue that can maintain the infrastructure and hence offset the cost of collection and disposal.

2.2.2 Solid waste management practices in Accra

Population and waste. Accra is both the political and the administrative capital of Ghana and the largest city in terms of urbanization among the ten leading centres in the country (Fobil et al., 2005). Like many cities in Sub-Saharan Africa, it is experiencing a rapid rate of growth. Its rate of urbanization makes it one of the fastest-growing cities in West Africa. As at 1997, the population of Greater Accra was estimated to be roughly 2.3 – 2.4 million people (IFPRI, 2000), and is envisioned to reach 4 million by 2020 (Grant et al., 2003).

The projected overall population growth rate in Accra at present is roughly 6% per year (Fobil et al., 2005). Accra covers 17,362.4 hectares, with the mean population density at present being 100 people per hectare.

The actual population densities vary from as few as 20 people per hectare in the new high-income areas to as many as 500 people per hectare in the most densely populated low-income neighborhoods (IFPRI, 2000). The increase in the population in Accra, has been fueled by intra-Ghana migration. This has resulted in housing deficit reaching 253,200 as at 2001 with a further 10% of Accra houses being listed as none upgradeable (Grant et al., 2003).

Collection and Transportation. Starting in 1997, solid waste collection and haulage was privatized and contracted out to 15 different companies. This is driven by the failure of the solid waste authority (WMD) to provide adequate solid waste collection and disposal services within the Accra metropolis.

Solid waste collection in Accra is either house-to-house collection or central container collection. House-to-house collection is most prevalent in the high-income communities and can range in cost from $2 to $4 per month, for weekly collection. House-to-house collection is scheduled to occur at least twice a week. The sliding price scale is based on the volume of trash collected per house. In densely-populated communities central waste depositories are located within 200 to 300m of residences and have daily collection at no cost. Recent estimates by the Department of Waste Management have house-to-house collection at only 20% of 2.3 million residents, while the remaining 80% dispose of their waste at community dumps, storm drainage channels, water bodies, and in open spaces.

The population of Accra generates 500-1800 tonnes of waste per day and this amount is expected to increase by 3.7 per cent annually in the metropolis. An average of 1,250 tons of solid waste is collected daily and hauled to a landfill site, 17 km west of Accra. This facility, an abandoned stone quarry site, has not been appropriately adapted to contain solid waste and at the moment it is the acceptable method of disposal (Armah, 1994 and Post et al 2003).

Waste stream information. Waste from domestic sources include, food waste, garden waste, sweepings, ash, packaging materials, textiles and metals. These waste fractions and their composition are presented in figure 2.3 below.

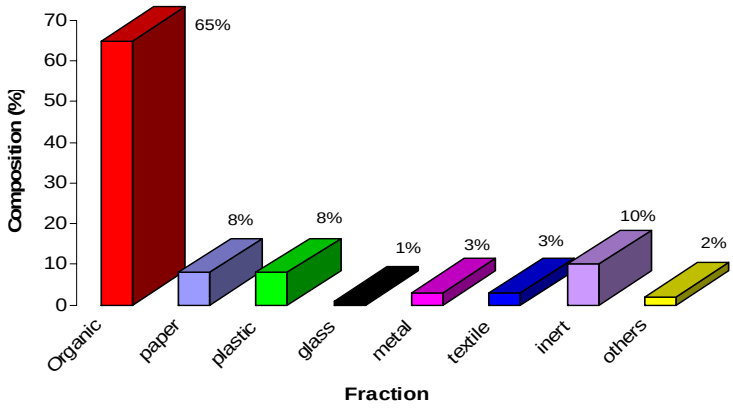


Figure 2.3. The waste components and composition in Accra metropolis (AMA, 2002**).**

According to the Waste Management Department of AMA in 2002, between 65 and 75 percent of waste is collected everyday over the past six years. Table 2.1 shows the average waste collection over the past 6 years.

Table 2.1. Volume and Daily tonnage of waste collected in Accra over the past 6 years.

Year	Average tonnage generated/day	Average tonnage collected/day
1998	750	450-600
1999	960	600-800
2000	1650	1200-1500
2001	1700	1300-1500
2002	1720	1300-1500
2003	1800	1300-1500

Source: AMA Waste Management Department (2002)

It has been observed that while the solid waste generation keeps increasing, the amount being collected remained the same (2000 to 2003). Accra Metropolitan Assembly source indicated in 2004 that the average solid waste generation has exceeded 1800 tons per day while the average daily collection has remained unchanged as the previous years at between 1200 and 1500 tons. The consequence of this left over solid waste is daily accumulation that has littered part of the Accra metropolis with the associated adverse environmental effects (Armah, 1994 and Anomanyo, 2004).

Disposal. The disposal systems are found in an unsuitable location and with no specific form of engineering, coupled with uncontrolled and non-ecological landfilling. The present dumping sites are not engineered to serve as sanitary landfill sites. Thus it constitutes a high potential for the spread of infections through run offs during rains and contamination of underground water. Between 1991 and late 2001, the AMA's Municipal solid wastes in the Accra metropolis were deposited at Mallam, a suburb of Accra. This dumping at Mallam site was however stopped in the late 2001 as the dump capacity has been exceeded and objections from nearby residents. Waste dumping was henceforth shifted to Djanman, a suburb of Accra, which unfortunately could not last as it was filled to capacity in just three months (WMD, 2002). These abandoned Mallam and Djanman sites are mountains of dumps and since they are neither landfills nor are there controls to check the spread of leachate and emissions, they are of great concern as a result of their threat to human health (Anomanyo, 2004 and JICA, 1999).

The current municipal solid waste dumping site is an old stone quarry site at Oblogo in the McCarthy Hills, 17 km west of Accra. Before it begun to be used in early 2002 there was an installation of clay lining but lacks an engineered containment of leachate. The AMA is only able to compact the waste to guarantee some level of proper dumping and hence "this site is considered a controlled dump rather than a properly engineered landfill" (Government of Ghana, 2003).

Since the formal systems of solid waste disposal cannot cope with the ever-increasing volume of solid waste being generated in Accra, the public itself employs various means of waste disposal. Waste is thus disposed off indiscriminately especially in watercourses and drainage channels and also through burning (Boadi et al., 2002). The consequence of dumping this untreated solid waste in an unsanitary landfill include; a total leaching of the organic fraction and other contaminants into ground water, uncontrolled anaerobic digestion at the dumpsite releasing methane and carbon dioxide into the atmosphere thereby increasing greenhouse gases. Incidences of malaria, diarrhoeal diseases, cholera, typhoid, infectious hepatitis and other infections of the gut are

always on the increase. The release of stench during raining season is unpleasant coupled with infestation of the area with snakes, rodents and flies makes life unbearable for people living close to the dumpsite (Chronicle, 2005 and Asomani et al 1999).

The remaining 10% to 15% of solid waste collected in Accra is composted. Composting in Accra occurs at the Teshie-Nungua Compost Plant, located east of the city centre and was established in 1980 by the Ministry of Local Government and the Accra Metropolitan Assembly. This facility composted more than 60 tons of domestic waste each day in 2000. The daily volume of composted trash has now reached between 125 and 188 tons per day. The waste composted at this facility has the following breakdown by weight: organic 85.1%, plastic 3.4%, glass 1.9%, metal 2.6%, paper 4.9%, and cloth 3% and is not separated. There are also some existing concerns about operational consistency and reliability at this composting facility. In addition, the compost has not been patronized by vegetable growers. This could be attributed to the poor quality of the fertilizer produced and therefore not suitable for vegetable cultivation in and around the city of Accra (Asomani et al 1999).

2.2.3 Effects of the inadequately managed solid waste

The sight and smell of poorly managed solid waste create a major discomfort to residents and visitors. Pollution of water resources increases the technical difficulty and cost of providing water supplies and the environmental health situation also has serious health impact, with attendant social and economic costs (Chronicle, 2004 and Asomani et al 1999). Flooding with its associated damage to public infrastructure and private property increases with improper solid waste management (Boadi et al. (2002).

Human health and social effects. The unsanitary conditions in and around parts of Accra has been the cause of the prevalence of cholera, malaria, diarrhoea and parasites (Chronicle, 2005). Anomanyo (2004) and Songsore et al. (1993) reported that 60 to 80% of diseases reported in the capital's hospitals and health centres are all environmentally related, predominantly around slums and where sanitation is poor. Among these diseases are malaria, diarrhoeal diseases, intestinal worms and upper respiratory diseases. Mosquito breeding grounds such as choked drains and gutters with stagnant waters are common. The high temperatures associated with the dumpsite at Oblogo (17 km away from Accra) speed up biodegradation of organic components of the waste producing landfill gases. The closeness of the dumpsite to the Densu River at Weija which is a source of drinking water to some parts of the Accra metropolis, and where treatment of this same drinking water takes place is of great worry.

Water pollution and flooding. Large volume of solid waste in the Accra metropolis creates a potential for the spread of infections through run offs during rainfall and contamination of underground water. It has been reported that serious leachate generations occur at the Mallam dumpsite usually after rains and leachate floods entering residents' compounds (Government of Ghana, 2003). These leachate contains pathogens and are a direct risk to human health and source of contamination to groundwater and surface waters. The dumpsite at Oblogo is within an earthquake-prone zone and such earthquake activities could allow leachates to easily contaminate underground water. Boadi et al. (2002) reported the devastation that occurred to lives and property in Accra, in 1995 due to floods which were partly attributed to accumulation of garbage which blocked the city's drainage channels. In addition, Boadi et al. (2002) cited the presence of domestic and industrial pollutants has increased the Biological Oxygen Demand (BOD) of the Korle lagoon. Sediments from the lagoon have revealed helminth identified as *ascaris* eggs, which require an ample supply of oxygen for development. This parasite is usually found where human waste disposal and sanitation practices are poor as it is the case of the Korle lagoon. Nyarko et al. (1998) stated that levels of heavy metals such as cadmium, copper and lead in the Korle lagoon was found to exceed the World Health Organization's recommended levels.

Impact on the aesthetic of the environment. Most of the containers for the community garbage have no covers, and always very full and overflowing to the ground (Appendix 1). As a result, it creates a very bad sight as it adversely affect the aesthetics of the environment.

Most often the overflown waste contains high amount of plastic bags which are blown about by the wind. There is an increase in indiscriminate dumping of plastic bags from so-called "pure water" hawkers. The litter makes the area unsafe and creates unsightly conditions in the environment. The litter and plastics bags make part of the metropolis very untidy and unhygienic. Government of Ghana (2003), reported that land and houses around the dumpsites have lost their value due to the bad conditions prevailing at the dumpsite which make people avoid such environments.

Potential problems associated with landfills: global perspective. Landfilling is still the most economical method of solid waste disposal in the world (Ustohalova et al., 2006). Despite the intensive efforts that are directed to recycling and recovery of solid wastes, landfills remain and will remain an integral part of most solid waste management plans (Al-jarrah et al., 2006). Modern sanitary landfills are designed with impervious liners, and leachate collection, removal, and treatment systems to minimize the potential for groundwater contamination. Hester and Harrison (1995), cited that even the most highly engineered containment landfills must be

expected to fail at some time in the future, whereupon leachate will be released. Despite the degradation of valuable land resources and the creation of long-term environmental and human health problems, uncontrolled, open dumping is still prevalent in most developing countries (Norbu et al., 2005).

It is a well known fact that the bioconversion or the natural biodegradation in landfills is a very slow process and may continue over scores of years and will require several decades to complete. In addition, ongoing anaerobic degradation in the landfills can take 20-40 years.
Several studies involving the degradation of wastes in release points provide evidence of leachate and biogas formation. These emissions are described below and are observed to be generated during long periods of time, even after the waste disposal ceases (Calvo et al., 2005; Parcy, 1999).

Emissions to the atmosphere. Municipal solid waste contains large fraction of putrescible organic matter which can be biodegraded by bacteria. The anaerobic degradation of these waste generates gases such as methane, carbon dioxide ammonia and hydrogen sulphide which slowly move into the atmosphere around the landfill. This affects the quality of air in the immediate vicinity and globally contributes to the greenhouse effect and global warming (Mata-Alverez, 2003).

According to Calvo et al. (2005) leachate and biogas are not the only emissions with potential negative impact, other impacts include, settlements in the landfill mass, odours, as well as dioxin, furan and other emissions of toxic gases, risk of explosion and fire, and noise and risks on public health. Methane and carbon dioxide are the main end products resulting from anaerobic digestion of organic matter in the ecosystem. Methane is known to contribute 25 times greater than carbon dioxide to global warming.

Chynoweth (1996) and Ustohalova et al. (2006) reported that the relative contribution of methane to greenhouse effect (parts per million volume basis) is estimated at 18% compared to 60% of carbon dioxide. Furthermore the significance of methane is influenced by the fact that the direct effect of methane is 21-fold greater than that of carbon dioxide (over a period of 100 years).

3 DEMAND FOR PRE-TREATMENT AND ANAEROBIC DIGESTION TREATMENT FACILITY

3.1 Background

The analysis presented so far suggests an immediate need for an alternative pretreatment option that would absorb the overwhelming amount of solid waste being generated in the Accra metropolis. Urban waste in Africa (Accra) is typically characterized by a high moisture content, high organic content and heterogeneity, which further complicates source separation. The prevailing technology and manpower does not facilitate treatment before landfilling. Landfilled waste with its high moisture and organic content contributes to the formation of leachate and landfill gas, which will create a long-term threat to the environment and public health. Under these circumstances, a simple and effective pre-treatment method of waste before it reaches a landfill or dumpsite is urgently needed. Biological pre-treatment of solid waste by simple anaerobic digestion has several advantages including lower concentrations of leachate requiring simpler treatment, a reduced aftercare period, reduction in landfill gas and less waste hauled to a landfill site (Norbu et al., 2005). When MSW is landfilled without pre-treatment emissions occur during and after the landfill operation in the form of approximately 150 m^3biogas/Mg MSW and 5m^3/ha/day of leachate, depending on the waste composition and climatic conditions (Stegmann, 2002). Carrying out pretreatment of the solid waste, the leachate pollution load could be reduced for Chemical Oxygen Demand (COD) and nitrogen compounds by 77% and 89%, respectively (Tränkler et al., (2002). Within 20 years, overall gas formation could be reduced by more than 35% and the global warming potential would be abated by more than 63%.

3.2 Advantages of anaerobic digestion of solid waste prior to landfilling

Waste stabilization and landfill space. Reinhart et al. (1998) explained that waste stabilization occurs more rapidly in controlled bioreactor treatment facilities than in conventional landfill as could be explained by the behaviour of waste that has undergone pre-treatment before landfilling and the one that has not been pre-treated before landfilling illustrated by figure 3.1 which indicates the advantages of having pretreatment applications as a function of pollutant load over the landfill operation time.

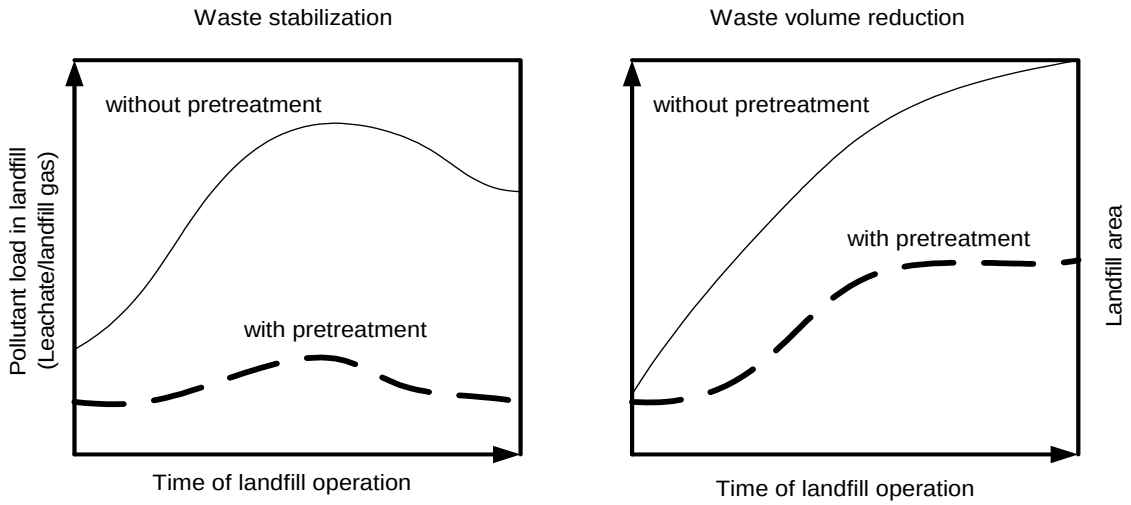


Figure 3.1. Waste stabilization and volume reduction with and without pretreatment.

As a result of faster stabilization and settlement in controlled bioreactors, less stabilized material would be produced, which means a smaller amount of waste would be landfilled. This will create more space for refilling as opposed to conventional dumping which takes a longer time to stabilize and therefore little or no refilling can take place. The change that would result from pretreatment prior to landfilling could create an additional 50% landfill space to accommodate more stabilized waste.

Controlled anaerobic digestion of solid waste generates more useful biogas as observed from results of experiments and field studies. Large volume of gas is harvested from the fast generation of gas from controlled anaerobic digestion compared to conventional dumping.

Reduced Environmental and social risks. One of the main aims of biological waste treatment is the fact that it is a natural process that is compatible with ecological processes. It has been observed that anaerobic digestion technology is generally perceived as a waste treatment technology that is a natural process used by man to protect the environment.

The higher rate of stabilization which occurs in controlled bioreactor implies that the environmental performance measurement indicators which are mainly gas composition and generation rate, leachate constituents and concentration would remain at very significantly reduced levels and would not pose much problem beyond the life time of the landfill. Also the stabilized anaerobic conditions in the controlled bioreactor would result in the immobilization of heavy metals into soluble forms while alkali metals form soluble nutrients in the leachates (Ecke et al., 2000). The harvesting of high energy methane as a source of clean fuel, instead of burning or allowing it to escape into the atmosphere, not only eliminates fire outbreaks but also reduces

the risk of its greenhouse effect. These reduced environmental impacts also improve social issues like reduced rate of diseases affecting animals, crops and humans.

3.3 Introducing anaerobic waste treatment facility

An initial feasibility study conducted on the waste stream composition revealed a high proportion of organic putrescible fraction. Based on the feasibility study, a planned site for vessel anaerobic treatment facility is conceived. In order to realize this plan of constructing an anaerobic digestion treatment facility, building of bioreactors could be made by using local available materials without the importation of expensive stainless steel reactor vessels. In addition, pipes, biogas collection facility/generator and liquid recirculation equipments are required. Causal loop diagram for the potential of anaerobic digestion of UMSW is illustrated through fig 3.2.

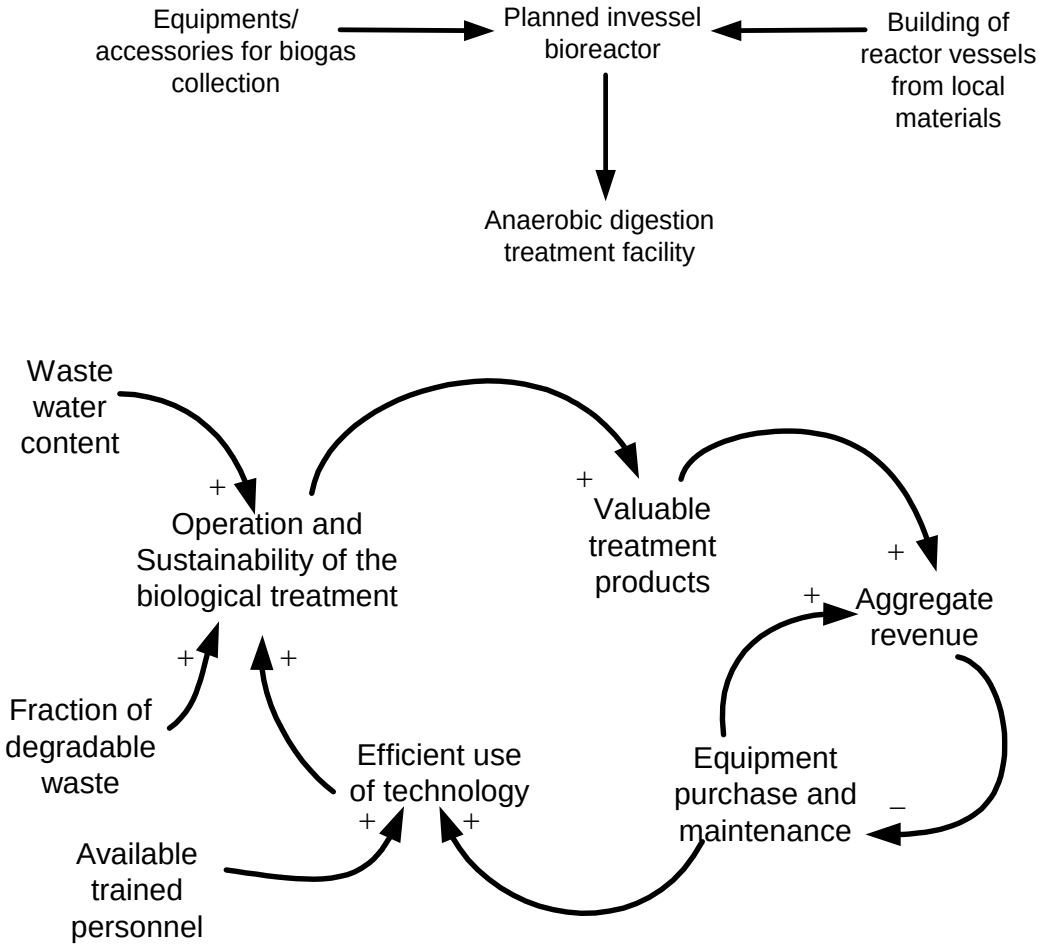


Figure 3.2. Causal loop diagram for the potential of anaerobic digestion of UMSW.

From figure 3.2, the nature of the incoming UMSW and the proper use of the technology determines the sustainability of the biological treatment system. High percentage of putrescible/degradable waste fraction and its moisture content promotes the use of the technology since these characteristics enhances the biological degradation process. The more moisture in the original feed indicates that less water has to be added. The availability of trained personnel and equipment supply determines the efficiency with which the technology is handled. The purchase of new equipment and maintenance is supported by the accrued revenue from the recovered biogas.

3.4 Proposed self-sustaining waste treatment model

3.4.1 Sustainable ecological park model

The flow diagram in figure 3.3 shows a desired sustainable ecological park model for treating unsorted municipal solid waste (UMSW) in the Accra metropolis through anaerobic digestion with material recovery and energy recovery facilities. From figure 3.3, the UMSW is fed to the AD unit, depending on the moisture content it might become essential to add some little amount of water to boost up the moisture content. Biogas is produced and the quantity of biogas produced is dependent upon the percentage fraction of the putrescible organic fraction of the overall input material. Feedstock (solid waste) is available in large quantities and expected to grow at 3.7 per cent annually in Accra.

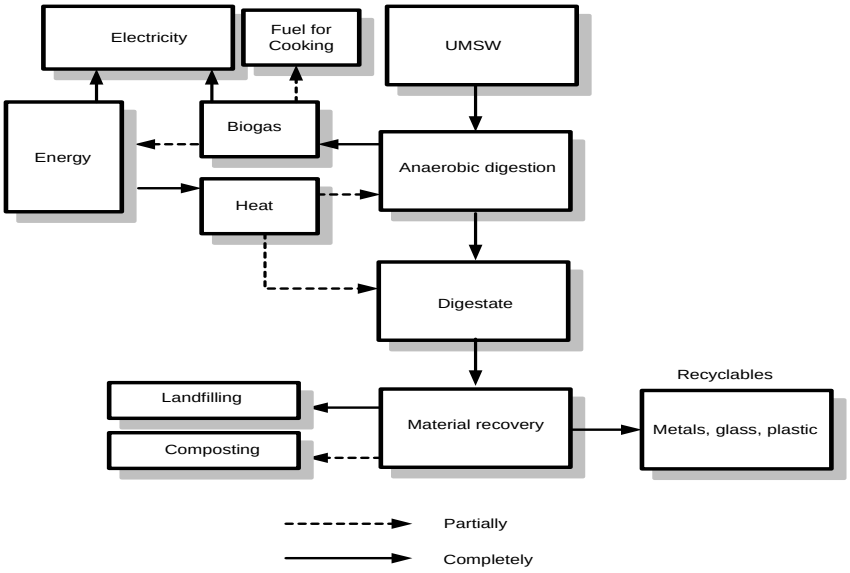


Figure 3.3. Desired eco-industrial park model for treating UMSW**.**

The produced biogas could be converted completely to electrical energy or partly to energy which is returned to the system to increase the digestion temperature as well as dry up the

digestate/stabilized material after the digestion process is over. The produced biogas could also be used directly as fuel for cooking in homes.

The tropical temperature conditions seem appropriate for efficient running of the digester without any additional heat coming from biogas conversion. Similarly, the digestate/stabilized material could also be dried by spreading it over an area under the tropical ambient temperature. The dried material could safely be sorted out to remove recyclable materials and the stabilized remaining organic material could be used as compost on agricultural fields. Alternatively, the overall digestate/stabilized material could be safely landfilled with little environmental consequences. The economic viability of the treatment facility cannot rest with gas production alone, so greater attention will be paid to obtaining a financial return from the digestate. The entire program would be self-sustaining as revenue would be generated from the sale of biogas/electrical energy and compost. Part of the accrued revenue could be used to pay workers, curtail depreciation cost and other logistics. Arrangements could be made with the various waste collection companies who will deliver their waste and pay tipping fees, this could also generate additional revenue.

3.4.2 Integrating the waste management systems

Figure 3.4 addresses the synergism of economic, environmental and social aspects of the proposed integrated solid waste management system.

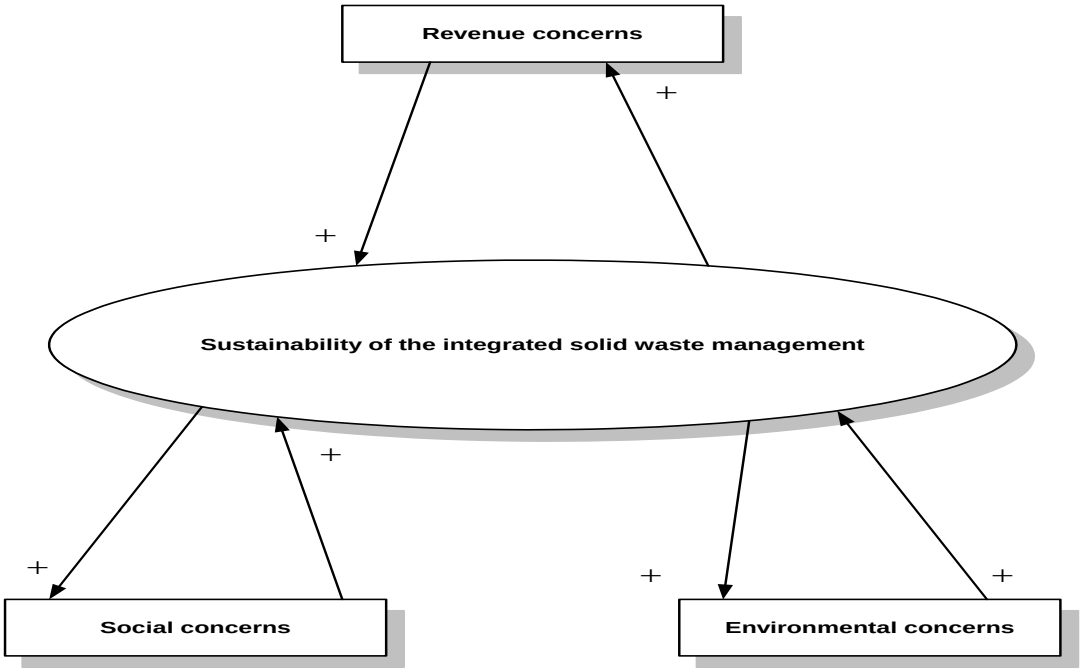


Figure 3.4. Synergistic interaction of economic, environmental and social concerns in the ISWM.

The economic aspect in terms of revenue generation is very vital as it ensures the self sustenance of the entire IWMS else the system will collapse due to insufficient funding. This is true in the sense that inadequate funding affects all spheres of the ISWM system including collection, transport as well as the continued running of the pre-treatment facility. The sustainability of the pre-treatment process equally depends on addressing both environmental (e.g. ground water pollution) and social (e.g. disease prevention) concerns.

4 ANAEROBIC DIGESTION OF MUNICIPAL SOLID WASTE: STATE-OF-THE ART

4.1 Background

High amount of MSW produced in both developed and developing countries presently represents one of the most important solid wastes generated by our society (Mata-Alverez, 2003). At present, about 1 million tons of organic wastes (wet weight) are digested per year world wide. These are converted to biogas on one hand, and a stabilized matter on the other hand (De Baere, 1999). Separate collection of MSW has increased significantly in most developed countries at present, and the clearest alternative treatment for the putrescent fraction coming from this recovery of waste components is the biological pathway (Bolzonella et al., 2003). In addition the current energy conservation policies as well as the strong demand for the reduction of atmospheric CO_2 emissions are in favour of the further development of advance AD techniques (Van lier et al., 2001).

Anaerobic digestion (AD), among the biological treatments, is cost-effective, owing to the high energy recovery linked to the process and its limited environmental impact, especially considering its limited greenhouse gas effect (Vogt et al., 2002). In terms of both ecological and economic status, various processes for treating biogenic (organic household wastes) wastes in plants have been compared (Mata-Alverez, 2003). The methane emissions were found to be greater (100-150 m^3 biogas per ton bio-wastes) from the context of life cycle analysis tools, following series of measurements at compost plants (Van lier et al., 2001). The results obtained from the measurements showed that anaerobic digestion had the advantage over composting, incineration or combination of digestion and composting, mainly because of anaerobic digestion's improved energy balance.

It has been reported that anaerobic processes will become much more important in the future for ecological reasons. Using global warming as a reference value for ecological balance, Mata-Alverez (2003), and Van lier et al. (2001) reported that anaerobic digestion scores much better than other options.

In summary, anaerobic digestion of solid organic wastes is today an established technology. However, its development is relatively recent.

4.2 Development and market for anaerobic digestion technologies

A lot of work has been published concerning the performance of different reactor configurations digesting organic solid wastes. Most of these publications focus more on the aspect of the anaerobic digestion of the putrescent fraction of municipal solid wastes.

Van lier et al. (2001) indicated in his study that, the request for more cost effective treatment systems for the growing food industry, combined with the occurrence of an international oil crisis, was the driving force that stimulated the most important research achievements of the seventies in the field of AD. In Europe for instance, a boost came from the Council of European Communities to grant financial assistance for projects in the field of alternative energy sources, including energy from waste (Ferrero et al., 1984).

Anaerobic digestion has become a proven technology for the treatment of organic wastes and on the side of the European Union has experienced much progress in anaerobic digestion and this technology has become a proven technology for the treatment of organic wastes (Van lier et al., 2001 and Mata-Alverez, 2003).

In Europe, over the past ten years, the treatment of OFMSW has increased from an overall capacity of 122,000 tons/year in 1990 to more than 1,000,000 in the year 2000 (De Baere, 2000). The available capacity of plant was 1,037,000 tons per year in 2000, and has risen dramatically to 2,553,000 tons per year in 2004 which reflects 150% increase over a four-year period (Lechner, 2005). The present AD plants in Europe and their capacities are shown table 4.1.

Table 4.1. Various anaerobic digestion plants in Europe at present (Lechner, 2005).

System	Number of plants	Capacity [tons/year]
BTA	9	213,000
KOGAS	16	215,500
DRANCO	10	234,500
BRV	12	517,000
VALORGA	11	786,700
Others	29	943,500
Sum	**87**	**2,910,200**

De Baere (2000), identified 53 plants (with a capacity larger than 3000 tons/year). Approximately, 60% of the plants operate at the mesophilic range and 40% thermophilic. A remarkable market has opened in the past few years for the digestion of ‘grey waste’ or ‘residual refuse’, i.e., waste that remains after source separation. Landfilling and incineration are the options for this fraction of waste. However, anaerobic digestion offers several advantages, such as, greater flexibility, the possibility of additional material recovery (up 25%), and more efficient in ecological energy recovery. The low calorific organic fraction is digested and the high-

calorific fraction is treated thermally. Also, the non-energy fractions can be recovered and reused (Mata-Alverez, 2003).

4.3 Current research on anaerobic digestion

Research activities continue on different aspects of anaerobic digestion of Organic Fraction of Municipal Solid Waste (OFMSW) despite the increasing number of full-scale plants presently available. This include activities from the fundamentals, including modelling of the process aspects (which is a very important tool for design), which include digester performance, inhibition problems, temperature influence, two-phase systems (Mata-Alverez, 2003).

Pavan et al. (2000a) biologically treated different mixtures of mechanically sorted and source-sorted organic fractions of municipal solid waste, which have different biodegradabilities. It was concluded that when digesting highly biodegradable wastes, such as source sorted OFMSW or fruit and vegetable wastes, it is advisable to use a two-phase anaerobic digestion system as this option allows much higher loads in the digester.

Using 'grey waste' as feed in the two-stage system, Scherer et al. (2000) achieved 80% degradation of volatile solids at temperatures of 65 ^{o}C in the hydrolytic stage at HRT = 4.3 d and 55^{o}C in the methanogenic stage with HRT = 14.2 d. Degradation rates obtained by the biogas yield (up to 797 L/kg VS fed) revealed up to 98% of the theoretical possible yield.

The influence of pH, organic load and hydraulic retention time on the process performance at mesophilic temperature of 35^{o}C was investigated by Raynal et al. (1998). The system involved several liquefaction laboratory-scale digesters with each treating one type of vegetable waste (potato peelings, green salad leaves, green beans mixed with carrots and apple pomice) and linked to a main fixed bed methane reactor. On average, hydrolysis yields were high up to 80%. A degradation rate of 80% was achieved in the methanogenic reactor for the mixed acidogenic effluent introduced. An average of 87% organic matter removal was achieved for average loading rates near 4 g COD l^{-1}.day^{-1} at a HRT of 17 days.

De Baere (2000), pointed out that on an industrial scale; one-phase systems for OFMSW digestion are absolutely predominant. Technical advantages reported seem not to be enough to justify a higher investment and higher maintenance costs.

Mesophilic and Thermophilic. Presently, there are considerable numbers of industrial digesters working at both mesophilic and thermophilic temperatures (De Baere, 2000). Both temperature ranges are possible for successful operation of a digestion and the choice is very much dependent on the kind of substrate handled (Pavan, 2000). Cecchi et al. (1991) pointed out that thermophilic temperature has been found optimal for digesting mechanically sorted OFMSW. However, many problems were encountered when treating source sorted OFMSW at 55^{o}C (Bernal et al., 1992).

Thermophilic treatment of source sorted waste was not adequate. In terms of biogas yield, thermophilic conditions have proved to be higher than that of mesophilic ones. Against surplus energy yield, thermophilic digestions obviously involve greater energy demand and thermal effort, which in many cases is comparable. Although yields and kinetics are more favourable at thermophilic temperature, optimal conditions depend on the type of substrate, i.e. biodegradability and the type of system (single/double-stage) employed (Vandevivere et al., 2003).

It is also suggested that two-phase operation is more advisable if thermophilic digestion is to be carried out when dealing with highly biodegradable substrate (Pavan, 2000).

4.4 Biological pre-treatment options (Anaerobic versus Aerobic)

When it comes to microbial degradation of organic waste, two alternatives comes to mind. These are aerobic degradation often referred to as composting, and anaerobic degradation. In aerobic degradation, oxygen is used as the final electron acceptor, and the main part of the energy in the organic substrate is made available to the cell, as the organic carbon is oxidised to carbon dioxide

Composting is considered to be the oldest technology for recycling of MSW and is still in use as a treatment process for solid waste prior to landfill. Among the feedstock that are composted include; separated MSW, UMSW, yard waste and co-composting of MSW with wastewater sludge (Tchobanoglous et al., 1993 and Lens et al., 2004). The economics of the composting process would be greatly enhanced if the compost produced can be sold. However, composting of MSW has not been considered as a promising pretreatment option due to the low quality of compost produced at the end of the process.

An important feature exhibited by the fermentative process that need to be mentioned is that, the stable final product is produced with a lower cell mass output. According to Pen-Varo (2002) and Björnsson (2000), only around 3 percent of the organic matter present in the influent water is converted to cell mass. The remaining 97 percent is converted via catabolism into CH_4 and CO_2 as stable end products. On the contrary, in aerobic systems, about 67 percent of the organic matter is converted through the anabolic process to cell mass while 33 percent is converted through the catabolic process into stable end product. Aerobic treatment of wastewater will result in large amount of biomass, the disposal of which can be expensive. The low biomass yield from anaerobic treatment and retention of energy in the methane are considered to be the main advantages of anaerobic digestion (Vandevivere et al., 2003).

Illustration of the fraction of organic matter converted through anabolism and catabolism according to Pen-Varo (2002) and Björnsson (2000), is presented in figure 4. 1.

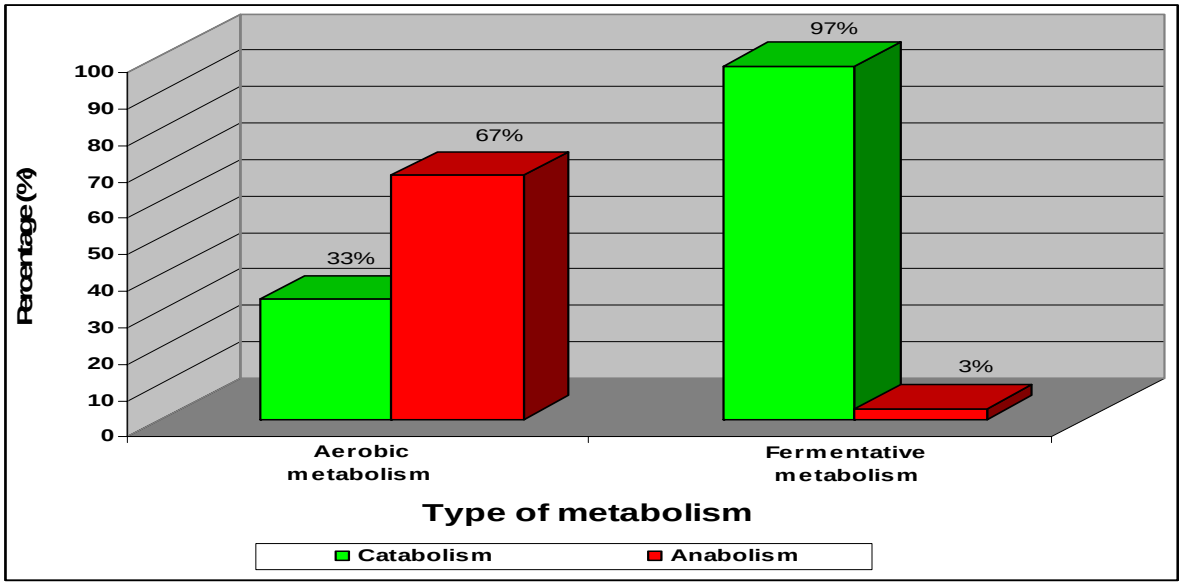


Figure 4.1. Fraction of organic matter converted through anabolism and catabolism in both conversional aerobic and anaerobic metabolism.

Besides the low small market available for the low quality compost produced, other factors such as the electrical energy input need to be considered. In anaerobic digestion, the total electrical energy produced exceeds the amount of energy used for the building and operation of the plant. In the composting process energy input is required in the order of 30-35 kWh per ton of MSW input, while anaerobic digestion is a net energy producing process that can generate energy in the range of 100-150 kWh per ton of MSW input.

For example, a plant treating 15,000 tons/year of organic fraction of MSW (OFMSW) by composting, around 0.75 million kWh/year of energy is needed, whereas for anaerobic digestion the net energy production is approximately 2.40 million kWh/year. The exact amount of energy yield depends on the quality of the OFMSW treated (Mata-Alverez, 2003). Similar yields referring to the experimental treatment of 100 kg of OFMSW is schematically presented by the flow diagram in figure 4.2.

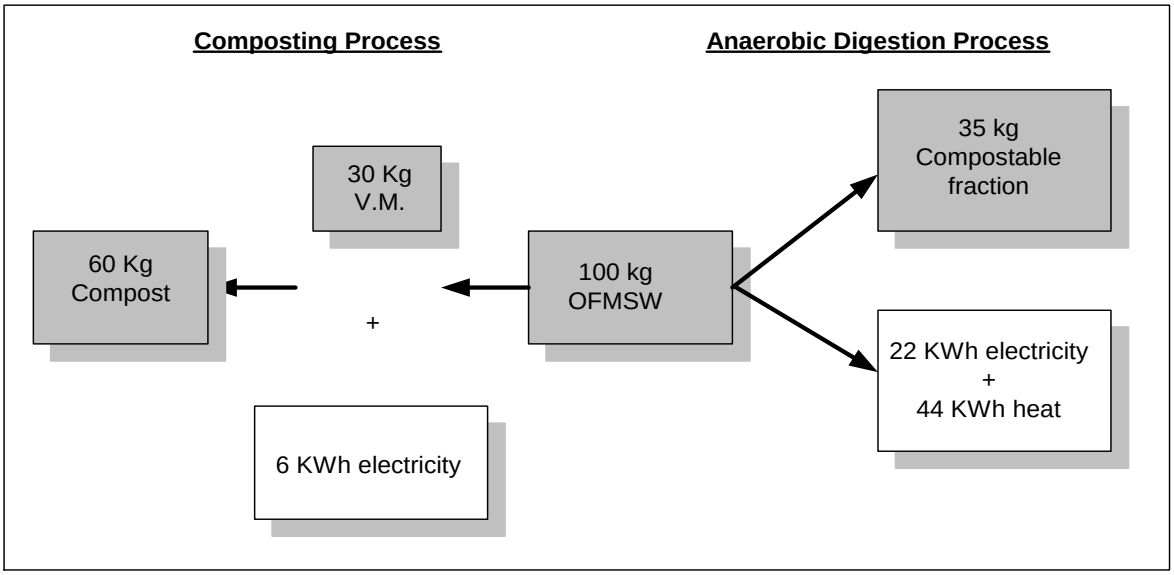


Figure 4.2. Yields of composting and anaerobic digestion technology for the treatment of 100 kg of OFMSW. (VM: vegetal matter) (Mata-Alverez, 2003).

4.5 Anaerobic digestion processes

4.5.1 Biochemical principles of anaerobic digestion

A general overview on the principles and some of the aspects of microbial processes in anaerobic digestion of organic waste is outlined below.

Bacterial metabolism. This refers to the mechanism which involves the removal of organic matter in a biological treatment system and is the most important among other processes. It refers to the use of the organic material either as a source of energy or as a source for the synthesis of cellular mass. There are two well-defined processes that characterize bacterial metabolism: ***Catabolism*** which occurs when organic matter is used as energy source and as a result transformed into stable end products; ***anabolism*** refers to the conversion and addition of the organic matter into cell mass. Both processes take place simultaneously because anabolism consumes energy and it is only possible when catabolism takes place simultaneously to supply the needed energy for cell synthesis.

Fermentative catabolism. This is a process that occurs in the absence of an oxidant element and it takes place with transfer of electrons. The following equation according to (Eckenfelder et al., 1966; Pen-Varo, 2002) describes the process of anaerobic digestion as:

$$C_x H_y O_z + \frac{(4x - y - 2z)}{4} H_2O \rightarrow \frac{(4_x - y + 2z)}{8} CO_2 + \frac{(4x + y - 2z)}{8} CH_4 \qquad 4.1$$

From equation 4.1, there is production of CH_4, which is the most reduced organic compound that exists. In this case, anaerobic digestion is regarded as the ultimate fermentative process. Carbon dioxide, which is a more oxidized compound, is also produced and both gases escape from the liquid phase as biogas. The released free energy from anaerobic digestion of acetic acid is equivalent to only 8 percent of the free energy released from oxidation of the same compound. The remaining 92 percent is kept as chemical energy in the form of CH_4. The analysis is presented by the following reaction equations:

$$C_2H_4O_2 + 2O_2 \rightarrow 2CO_2 + 2H_2O + 207kcal \quad 4.2$$

$$C_2H_4O_2 \rightarrow CH_4 + CO_2 + E_{dig} \quad 4.3$$

The E_{dig} = free energy release from reaction 4.3 can be calculated by considering firstly free energy released during methane oxidation according to the following equation

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + 191\ kcal \quad 4.4$$

Now, combining equation 4.2 and 4.3 reaction (4.1) is obtained and the result of the free energy balance:

$$E_{dig} + 191 = 207\ kcal/mol \qquad E_{dig} = 16\ kcal/mol$$

Anabolism. Anabolism is a biological process that results in the growth of the bacterial mass and it can be measured by the increase in the volatile solids concentration. But catabolism can be estimated by methane production. The overall combined effect of the two processes can be determined from reduction in the substrate concentration (organic matter). The yield coefficient (Y) correlates to the bacterial mass formed from anabolic activity and metabolized mass of organic material by the equation.

$$Y = -\frac{dX}{dS} \quad 4.5$$

Where Y being the yield coefficient, X is the volatile solids concentration (biomass) and S represents the organic matter concentration.

Bacterial decay. Bacterial growth is controlled by the abundance or lack of nutrients and electron acceptors as well as the production and accumulation of inhibitory metabolites. Their death or lysis, produces substances that are incorporated into the biodegradation cycle. The kinetics of this decay process is usually expressed as being proportional to the biomass concentration by means of the decay coefficient K_d:

$$\left(\frac{dX}{dt}\right)_{decay} = -K_d X \quad 4.6$$

Anaerobic degradation of organic fraction of municipal solid waste proceeds in the absence of oxygen and the presence of anaerobic microorganisms (Ostrem, 20004). Anaerobic digestion

process requires the concerted action of a highly varied microbial population, consisting of several groups of strict and facultative bacteria strains (Mata-Alverez, 2003; Pen-Varo, 2002). It occurs in four metabolic stages, hydrolysis, acidogenesis, acetogenesis and methanogenesis (Veeken et al., 2000).

4.5.2 Metabolic stages of anaerobic digestion

Hydrolysis. In the first process, hydrolytic microorganisms secretes an enzyme (cellulase, amylase, lipase or protease) which hydrolyses polymeric materials to monomers such as glucose, amino acids and fatty acids. Also the microorganisms producing these enzymes can be obligate or facultative anaerobes. It is commonly found that hydrolysis is the rate-limiting step in degradation when the substrate is in the particulate form (Ghaly et al., 2000 and Borja et al., 2003).

Acidogenesis. Soluble substances including hydrolysis substances products are subsequently converted to higher volatile fatty acids, H_2 and acetic acid by a second group of microorganisms called the fermentative acidogenic bacteria, e.g., *Clostridium spp* (Veeken et al., 2000; Pen-Varo, 2002). These organisms comprise a wide variety of different bacterial genera representing both obligate and facultative anaerobes, and acidogenesis is often the fastest step in the anaerobic conversion of complex organic matter in liquid phase digestion (Björnsson, 2000). The acidogenic microorganisms prefer a slightly acidic environment (pH 4.5-5.5) and are less sensitive to changes in incoming feed stream (Ostrem, 2004).

Acetogenesis. The products from this stage vary with the type of bacteria and environmental conditions (i.e. temperature, pH and redox potential). In a stable anaerobic digestion, the acetate and H_2-producing bacteria called acetogenic bacteria (e.g. *Syntrobacter wolinii* and *Syntrophomonas wolfei*) transform the products of acidogenesis into acetate, hydrogen and carbon dioxide which are substrate for the methanogens. Approximately, 72 per cent of the influent COD is converted to acetate. There may be formation of carbon dioxide or hydrogen along with the acetate depending on the oxidation state of the original organic matter (Veeken et al., 2000; Pen-Varo, 2002).

Methanogenesis. Finally, the last group of microorganisms, the methanogenic, produced methane from acetic acid, hydrogen, and carbon dioxide as well as directly from other substrates of which formic acid methanol are the most important (Veeken et al., 2000).

A flow diagram of the main process steps of anaerobic digestion according to Sharma et al. (1988) and Verma (2002), is shown in figure 4.3.

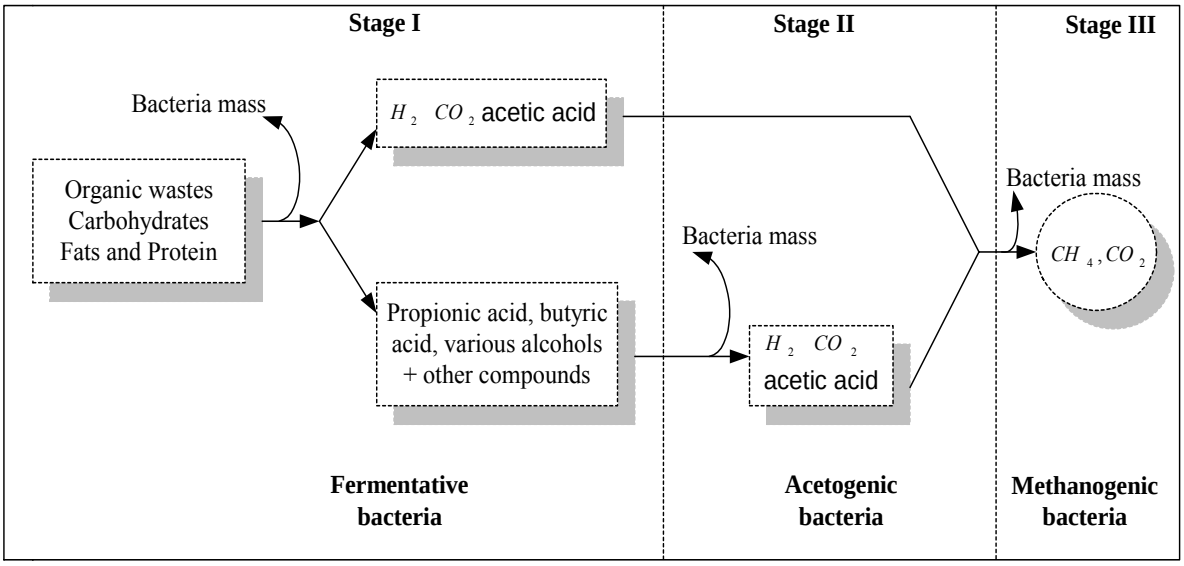


Figure 4.3. Multi-step anaerobic degradation process.

The methanogenic state comprises the production of CH_4 from acetate or from the reduction of CO_2 by acetotrophic and hydrogenotrophic methanogens (Pen-Varo, 2002) according to the following reactions:

$$CH_3COOH \rightarrow CH_4 + CO_2 \quad 4.7$$

$$CH_3COOH + 4H_2 \rightarrow 2CH_4 + 2H_2O \quad 4.8$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad 4.9$$

Generally, the composition of the biogas depends on the mean oxidation state of the carbon in the substrate. The more reduced the carbon, the higher the ratio of methane to carbon dioxide as reported by Gujer and Zehnder (1983). The mean oxidation state of carbon fixed to carbohydrates, proteins and lipids is about 0.0 to -0.6 and -1.4 to 1.8, respectively. Anaerobic digestion of carbohydrates yields an equal molarity of methane and carbon dioxide. Decomposition of proteins and lipids results in up to 65 and 75 percentage volume of methane respectively (Ecke et al., 2000).

The most common acetoclastic methanogens found in reactors treating substrates with high volatile fatty acid concentration are the genera *methanosarcina* and *methanosaeta* formerly called *methanothrix.* It was reported that, *methanosarcina spp* were identified as rods and are the most dominant bacteria while *methanosaeta spp* are long filamentous species (Burak et al., 2002

and Pen-Varo, 2002). Mata-Alverez, (2003) reported that both have a slow growth rate and a doubling times of around 24 hours.

The hydrogen-utilizing methanogens help to maintain low partial pressures needed for conversion of volatile fatty acids and alcohols to acetate by the acetogenic bacteria. These methanogens converts H_2 and CO_2 into CH_4 according to equation 4.9. There is a synergistic relation between the hydrogen producers and hydrogen scavengers. Small variation in H_2 concentration can change the products of the acid-forming phase. As the partial pressures of H_2 rises, H_2 oxidation becomes more thermodynamically favorable than acetate degradation and acetate concentration is increased. Degradation of other substrate (alcohols) is also inhibited by high hydrogen concentrations.

The overall hydrogen partial pressures are below 10^{-4} atm for stability and good performance in anaerobic digestion systems and this correspond to a 10^{-8} M solution (Pen-Varo, 2002).

4.5.3 Post treatment.

After the completion of the anaerobic digestion, the remaining biodegradable organic material (known as digestate or effluent) is subjected further to post treatment processes. This includes dewatering, aeration and leachate treatment. It is usually dewatered to 50 – 55% TS with screw press, filter press or other types of dewatering systems. The importance of aeration process in post treatment is to remove the left over biodegradable organics by aerobically reducing the organic compounds to valuable material compost which is used as soil conditioner. After this point, the compost can be further cleaned by screening, to remove unwanted material such as small pieces of glass or plastic. The pressed liquid, which may contain high concentrations of volatile fatty acids, is centrifuged, recycled or sent to wastewater treatment (Ahring, 2003b).

4.5.4 Kinetics of anaerobic digestion

The relation between the velocity at which a reaction occurs and the substrate utilization rate is referred to as kinetics (Pen-Varo, 2002). The effectiveness of AD depends on the kinetics of the respective conversion processes. Anaerobic kinetics are influenced by a number of intensive properties (Ecke et al., 2000).

A lot of expressions have been formulated to describe the kinetics of microorganisms metabolism based on the Monod model. The Monod model has been widely accepted and used in biological treatment because of its mathematical simplicity and relative easiness in estimation of the kinetic parameters (Garcia, 2003).

Accoding to Mata-Alverez (2003); Pen-Varo (2002), and Ecke et al. (2000) previous work found Monod kinetics reasonably satisfactory for methanogenesis in anaerobic digestion.

Monod suggested that the bacterial growth rate (μ) is not constant but a function of substrate concentration (S) which then becomes a limiting factor for culture growth established the expression

$$\mu = \mu_{\max}\left(\frac{S}{K_s + S}\right) \qquad 4.10$$

Where μ_{max} is the maximum specific growth rate (d^{-1}). The 'half-saturation constant' (K_s in mgCOD/l) expresses the value of substrate concentration for which μ takes the value of $\mu_{max} / 2$. For very high values of S (excess of substrate), the ratio (S / Ks + S) approximates unity or the bacterial growth rate becomes a zero order in S,

$$\mu = \mu_{\max} \qquad 2.11$$

In other words, it becomes independent of the substrate concentration. Maximum specific growth rates of *methanosaeta spp* and *methanosarcina spp* (acetate consuming bacteria) to be $\mu_{max} = 0.1$ and 0.3 d^{-1} respectively. For these same species, also reported Ks values of 30 and 200 mg/l acetate respectively.

For values of S much smaller than K_s (limiting substrate conditions) the Monod expression leads to a first order kinetics in S:

$$\mu = \frac{\mu_{\max}}{K_s} \bullet S \qquad 4.12$$

As a result, μ affects the growth kinetics by different weight depending on the value of S in the reactor, relative to Ks.

A minimum substrate concentration is required in order to maintain a steady state bacterial growth in the reactor; therefore $\mu_{max} \geq K_d$. Mathematically, this phenomenon can be written in consideration with equation 4.10 as

$$K_d = \mu_{\max} \bullet \left(\frac{S}{K_s + S}\right) \qquad 4.13$$

Solving for S,

$$S_{\min} = \frac{K_s K_d}{\left(\mu_{\max} - K_d\right)} \qquad 4.14$$

Where S_{min} is the lowest value of substrate concentration which can be obtained in the treatment system. And this equals to the sum of the minimum concentrations of all the different processes taken place in the digester. Furthermore, the lowest minimum effluent substrate concentration can not be achieved under any environmental conditions.

In practice, the effluent substrate concentration may be greater than the minimum achievable because otherwise a very long retention time would be required.

Due to this fact, there will be a net growth of cellular mass within the reactor and after sometime of operation, the system will become full of biomass. If the wastage is equal to the net production rate of sludge then a constant biomass concentration will be established in the reactor.

A very important operational parameter, the sludge age, or the average residence time (θ_s), is related to the effluent substrate concentration and it is given by the following ratio.

θ_s = mass of solids in the reactor/solids wastage

Considering the mass balance for a steady-state reactor without accumulation of biomass gives

$$\left(\frac{dx}{dt}\right)_w = \left(\frac{dx}{dt}\right)_y + \left(\frac{dx}{dt}\right)_d \qquad 4.15$$

$$X/\theta_s = X\mu - XK_d \qquad 4.16$$

Solving for θ_s

$$\theta_s = \frac{1}{(\mu - K_d)} \qquad 4.17$$

Where X = biomass concentration (mg VSS/l), μ = Specific growth rate (d^{-1}), K_d = decay rate constant (d^{-1}), θ_s = sludge age (d^{-1}) and w, g, d = waste, growth and decay respectively.

Substituting μ from equation 4.17 into equation 4.10 gives

$$S = K_s(K_d + \frac{1}{\theta_s}) / \left[\mu_m - \left(K_d + \frac{1}{\theta_s}\right)\right] \qquad 4.18$$

From equation 4.18, it is observed that the effluent concentration depends on the values of the three kinetic constants (K_s, μ_m, K_d) and the sludge age θ_s as a process variable. And the minimum sludge age (θ_{sm}) can be calculated from equation 4.18, when effluent substrate concentration is equal to the influent concentration. This occurs when there is no conversion of organic matter. Also, the influent substrate concentration is much higher than Ks value, so that removal of organic matter takes place. Therefore, equation 4.18 simplifies to;

$$\theta_{sm} = \frac{1}{(\mu_m - K_d)} \qquad 4.19$$

Further substituting equation 4.19 into 4.14 the minimum substrate concentration (S_{min}) in terms of θ_{sm} is obtained as shown in equation 4.20.

$$S_{\min} = K_s K_d \theta_{sm} \qquad 4.20$$

Hence equation 4.20 shows the relationship between S_{min} and θ_{sm} that is substrate specific and represents the lower limit of the effluent substrate concentration essential for adequate process operation. It is concluded that the sludge age or average sludge residence time (θ_s) is an operational parameter, which can be used as a selective factor by imposing stress on bacterial consortium.

Kinetic model for particulate matter utilization. Vavilin et al. (1996) compared four types of hydrolysis kinetics (first-order, Monod, Contois and the two-phase taking into account colonization of the particles by bacteria). It was observed that all the types of hydrolysis kinetics could fit a variety of experimental data comparatively well, in that it justifies the broad application of the first-order kinetics and as such suggests it as the simplest way to describe the hydrolysis rate.

The first-order kinetic model is more appropriate for complex wastes such as the OMSW where hydrolysis plays an important role (Pavan et al., 2000). Solid hydrolysis is the rate limiting step in anaerobic digestion of cellulose (Kübler et al., 1994). Therefore to enhance the anaerobic degradation the conditions for hydrolysis have to be improved.

In the anaerobic digestion, solid forms of biomass are converted into liquid forms by using hydrolyzing microorganisms. As a result liquid are enriched with carbon compounds which is designated as COD. These carbons are then converted into gaseous form such as methane and carbon dioxide by using microorganisms. Some amount of it is used for cell growth and maintenance. So solid carbon particles are converted into gaseous carbon through liquid carbon which is the main substrates for the methanogenesis.

The following major reaction steps are involved in the anaerobic digestion of particulate matter to methane.

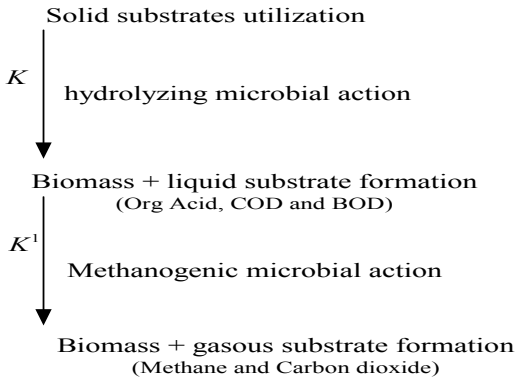


Figure 4.4. A scheme of the anaerobic degradation process

Assuming the first order degradation pattern was followed by hydrolytic process, then, the rate of degradation of particulate organic matter can be written as

$$-dc/dt = KC$$

$$With:$$

$$-dc/C = Kdt$$

$$It\ follows:$$

$$\ln C/C_o = Kt$$

$$\Rightarrow$$

$$C = C_o * \exp^{(-kt)} \qquad 4.21$$

$$Where,\ C = Substrate\ concentration\ at\ time\ t\ in\ g/litre,$$

$$C_o = Initial\ substrate\ concentration\ in\ g/litre\ and$$

$$K = Rate\ cons\tan t\ in\ days.$$

$$Further\ \text{int}egration\ wrt\ t\ leads\ to$$

$$\frac{dC}{dt} = \left[C_o \cdot \exp^{(-k_H \cdot t)}\right]dt \qquad 4.22$$

$$Finally\ gives$$

$$C = C_o\left(1 - \exp\left(-k_H \cdot t\right)\right) \qquad 4.23$$

Parameter values for C_o and K_H of (equation 4.23) could be estimated using nonlinear least-squares curve fitting of the experimental data of the COD by spreadsheet program Excel.

Similarly, assuming first order degradation of substrate (COD) according to Mace et al. (2003), the production of methane is assumed to follow:

$$ds/dt = -K \cdot S \qquad 4.24$$

Where K is the first-order constant and S the biodegradable substrate concentration. Taking into account the existing relation between S and methane production.

$$\left(B_o - SMP\right)/B_o = S/S_o \qquad 4.25$$

Integrating, the following equation is obtained:

$$\left(B_o - SMP\right)/B_o = \exp\left(-kt\right) \qquad 4.26$$

where SMP is the methane production per kg of VS fed, B_o the same parameter but measured after an infinite digestion time, that is the ultimate methane yield.

A mass balance applied to a continuous flow digester of volume V and a feed flow rate Q, yields:

$$QS_o - QS = VkS \qquad 4.27$$

Taking into account equation (4.25) and the HRT $=V/Q$, Equation (4.27) leads, after rearrangement, to the following expression:

$$1/SMP = 1/B_o + 1/(B_o \cdot HRT \cdot k) \qquad 4.28$$

A regression of 1/SMP versus 1/(HRT) gives B_o and K.

And

$$SMP = B_o/(1 + 1/(HRT \cdot K)) \qquad 4.29$$

Some general conclusions can be drawn from equation 4.29. At higher HRT, more biogas will be produced and the closer SMP will approach B_o.

4.6. Process parameters and influencing conditions

4.6.1 Process functioning and performance

The entire treatment process in an anaerobic degradation is described by the basic mechanism illustrated in section 4.5.2. However, it is useful to present the synergy of parameters affecting the overall anaerobic digestion process.

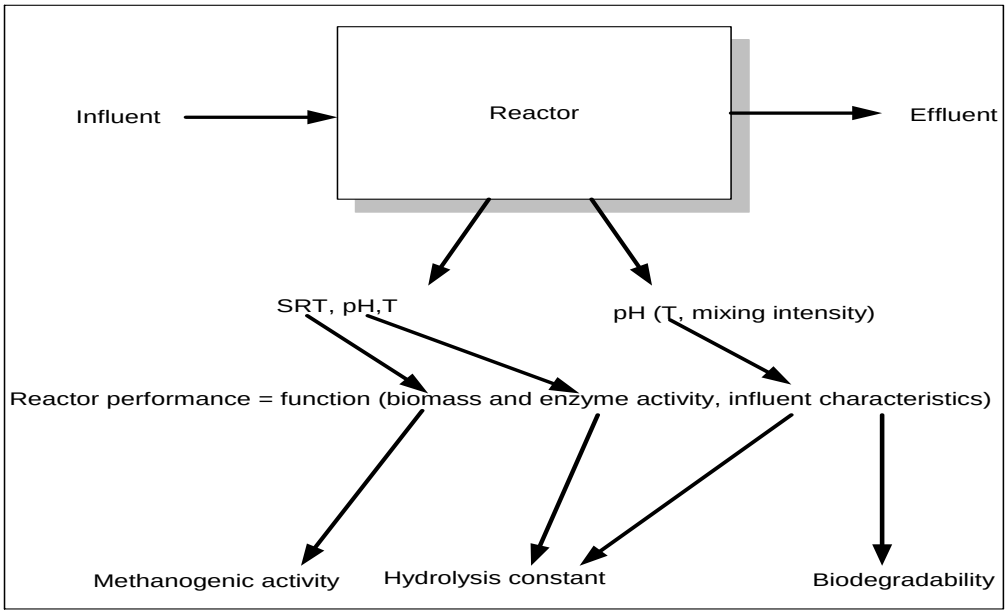


Figure 4.5. The relationship between reactor conditions, performance and measurable parameters.

A scheme of the relationship between reactor conditions (SRT, pH, T), performance of the reactor which is a function of biomass, enzyme activity and influent characteristics giving rise to measurable parameters such as methanogenic activity, first-order hydrolysis constant and biodegradability is shown in figure 4.5 according to Sanders et al. (2003).

Various levels of volatile solid (VS) destruction efficiencies and gas production rates have been reported ranging from 40%-60% and from 230 l CH_4/kg VS – 330 l CH_4/kg VS respectively. Gas composition range 50% CH_4 – 60% CH_4 on dry volumetric basis has been reported (Stenstrom, 1983).

4.6.2 Environmental conditions affecting the process

The complexity of anaerobic degradation reflects the biological part of an ecosystem that is also strongly influenced by chemical and physical parameters that are referred to as environmental factors (Björnsson, 2000). With respect to the anaerobic digestion technology, most essential factors include the temperature, pH and buffering systems, nutrient requirement, and the presence of toxic substances in the process (Diaz, 1993).

Temperature. Generally, the rate of all reactions varies with temperature. In biological systems, temperature increase is not as great as for chemical reactions. Methane production has been documented under a wide range of temperatures, but bacteria are most productive in either mesophilic conditions 25-40 ^oC, or in the thermophilic conditions, at 50-65 ^oC (Ahring, 2003 and Ostrem et al., 2004). A mesophilic digester must be maintained between 30^oC and 35 ^oC for optimal functioning. Where as a thermophilic digester must be maintained between 50^oC and 55^oC. Cecchi and Pavan et al. (1993) observed that temperature is a factor that affects the kinetics and the composition of the mixed microbial population. Ecke (2000), described that microorganisms act as biocatalyst. Enzymes catalyse the metabolic reactions in a way which can be described by the Michaelis-Menten equation:

$$V = \frac{K_{cat} S_o E_o}{K_m + S_o} \qquad 4.30$$

Where V is the product formation rate, K_{cat} is the turn over number, K_m is the Michaelis's constant and S_o and E_o signify the initial concentrations of substrate and enzyme respectively. Both K_{cat} and K_m depend on temperature. K_{cat} is defined according to the Arrhenius equation;

$$K_{cat} = Ae^{-\Delta G^* / RT} \qquad 4.31$$

A is a constant and ΔG^* is the enzyme-substrate activation energy. A and ΔG^* are always greater than zero, therefore K_{cat} increase with temperature.

The graphical illustration in figure 4.6 shows the direct relationship between the temperature and the rate of anaerobic digestion (Mata-Alvarez, 2003). Two optimal temperatures of 55 and 35 ^{o}C for thermophilic and mesophilic respectively were identified. A thermophilic temperature range was observed to reduce the required retention time. The microbial growth, digestion capacity and biogas production could be enhanced by thermophilic anaerobic digestion since the specific growth rate of thermophilic bacteria is higher than that of mesophilic bacteria.

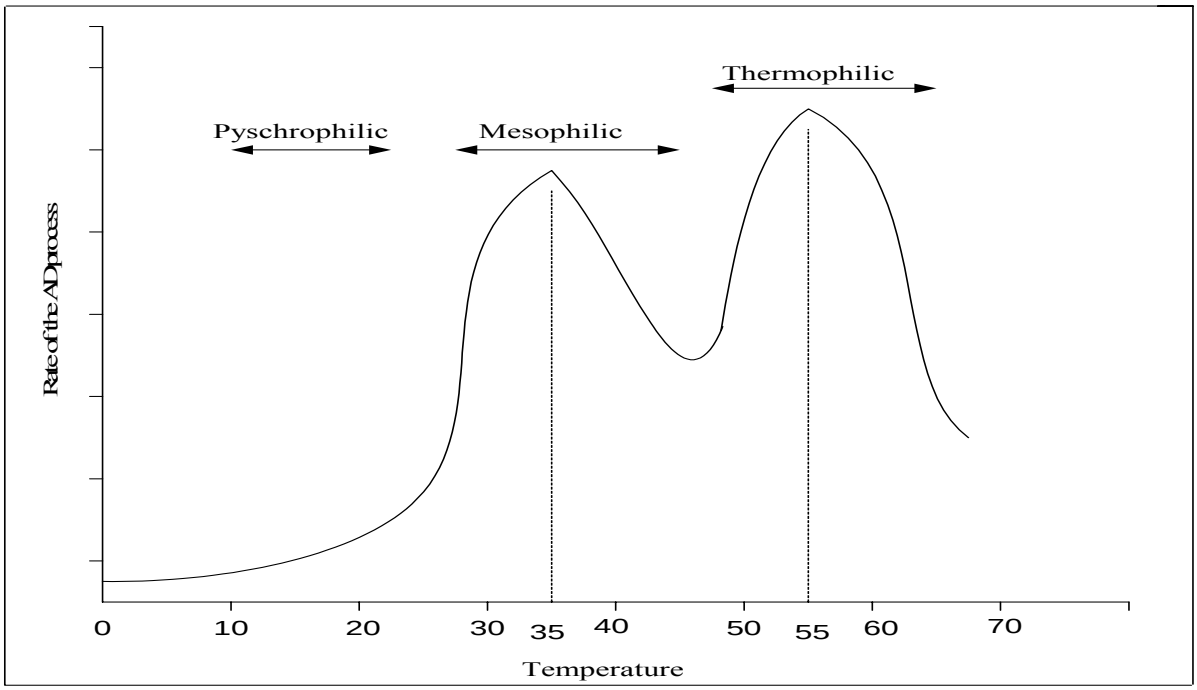


Figure 4.6. A scheme of the rate of anaerobic digestion at the various temperature ranges (adapted from Mata-Alverez, 2003).

Conversely, in a review, according to Ecke (2000), the majority of known methanogens are mesophiles and this could be the reason for the observation that mesophilic operation is more robust. Nevertheless, in adapting the process design temperature is not necessarily a limiting factor in applying anaerobic digestion, but rather temperature stability (Van Lier et al., 1997).

Björnsson (2000), reported that a change from mesophilic to thermophilic conditions results in an immediate shift in the methanogenic population due to rapid death of the mesophilic organisms. Methanogenesis is possible under psychrophilic conditions (temperatures below 20^{o}C), in order to achieve reasonable methane production, the temperature should be above 20^{o}C, and this fact makes anaerobic treatment more attractive in the tropical countries (Björnsson, 2000; Pen-Varo, 2002). Other authors have claimed success with the anaerobic digestion of waste at ambient temperature, which is known to be cost effective (Biey et al., 20003). Temperature has a positive effect on digestion rate, resulting in higher volumetric methane production rate (Ecke et al.,

2000). It has been observed that methanogenic rate in refuse increased 2.6 times when the temperature was increased from ambient temperature to 30 ^{o}C and a further 3 times when the temperature was increased from 30 to 40 ^{o}C (Ahring, 2003). Also, Björnsson (2000), reported that the extracellular enzymatic hydrolysis of particulate matter is slow at lower temperature ranges of 10 – 15 ^{o}C.

In addition, it has been realized that, there is direct relationship between temperature and organic loading rate. This means that, when temperature is decreased loading must simultaneously decrease to maintain the degree of treatment (Ahring, 2003; Pen-Varo, 2002).

pH. The anaerobic digestion is limited to a relatively narrow pH interval from approximately 6.0 to 8.5; a pH outside this range can lead to imbalance. Each of the microbial groups involved in anaerobic degradation has specific pH optimum and can grow in a specific pH range (Ahring, 2003). The methanogens and acetogens have pH optimum at approximately 7, while acidogens have lower pH optimum around 6. Methanogens at pH lower than 6.6 grow very slowly (Mata-Alverez, 2003; Björnsson, 2000).

The commonly occurring acid/base in anaerobic digesters with their pK_a values in water at 25^{o}C according to Björnsson, (2000) are presented in table 4.2 below.

Table 4.2. Commonly occurring acids/bases in anaerobic digesters and their pK_as.

Compound	pK_a
VFAs	4.7- 4.9
Carbonic acid	6.3
Hydrogen sulphide	7.1
Dihydrogen phosphate	7.2
Ammonium ion	9.3

From table 4.2, the compounds that have a significant buffering capacity (referred to as alkalinity) in the useful functional region around pH of 7 include carbonic acid (bicarbonate), hydrogen sulphide, dihydrogen phosphate and ammonia.

The presence of buffering compound depends on the composition of the substrate and the total organic load. It has been observed that, the alkalinity needed to maintain pH is largely governed by the carbonate equilibrium. High alkalinity through the production of ammonia is generated from waste containing high concentrations of nitrogen components. If the sulphide system present is generally very low compared with that of carbonate; the buffering contribution of sulphide is usually negligible. As a recommendation procedure, if the pH in the anaerobic

digester should decrease, feeding must stop and the buffering capacity should increase through the following; adding of calcium carbonate, sodium bicarbonate or sodium hydroxide. This indeed is an expensive way of dealing with the problem, and a better alternative is to avoid the accumulation of VFAs by suitable process design and operation (Björnsson, 2000). Also, the pH determination is really useful; it is absolutely poor by itself and is important to relate its value to other process parameters, e.g. alkalinity, VFA concentration, and biogas production and composition (Mata-Alverez, 2003).

Nutrients. Organic and inorganic substances are necessary for anaerobic digestion process to run optimally. Osuna et al. (2003) reported that suboptimal metal concentrations may render the anaerobic degradation process inefficient. On the contrary, beyond a certain threshold level it can be inhibitory. An average COD/N/P ratio of around 600/7/1 can be recommended for substrates to be an aerobically digested (Mata-Alverez, 2003). Alphernaar et al. (1993) suggested a minimum C:N:P ratio of 100:28:6.

OFMSW usually contains nutrients and micronutrients in adequately high quantities for microorganism growth not to be limited (Ecke, 2000; Mata-Alverez, 2003). When considering the treatment of single waste or wastewater fractions, the degradation can be limited by the availability of nutrients (Björnsson, 2000; Mata-Alverez, 2003). Speece (1987), observed that other nutrients such as sodium, potassium, calcium, magnesium, chloride and sulphur are required in lower concentrations. Other micronutrients required by the microorganisms have been identified. This includes; nickel, molybdenum, zinc, vanadium, copper and iron. Presently there is no universal recommendation for nutrient concentrations that can be given because they are strongly dependent on the actual circumstances at which the AD is performed (Ecke, 2000).

Toxic substances. A number of compounds are toxic to the anaerobic microorganisms. Methanogens are commonly considered to be the most sensitive to toxicity in anaerobic digestion (Ahring, 2003). Inhibition can be caused by substances either entering with influent substrate or being produced by the anaerobic process itself. Regarding the latter, a simple classification could be substrate inhibition, where the substrate provokes enzymatic inhibition or product inhibition, which is caused by products that are final intermediates in the chain of simultaneous biochemical reactions, such as NH_3, H_2S and volatile fatty acids. These substances are pH dependent since only the nonionised forms exhibit microbial toxicity.

- ***Ammonia (NH_3).*** Ammonia is toxic at pH greater than 7 which implies that inhibition is a function of total ammonia and pH as expressed by the equilibrium equation below.

$$NH_4^+ \leftrightarrow NH_3 + H^+ \qquad pKa = 9.3$$

The higher the pH, the higher the concentration of free ammonia. At pH 7 the ionized form dominates, and only 1% is in the form of free ammonia, while at pH 8, 10% is in the unionized form. In unadapted cultures, free ammonia, level of 150 mg/l can cause growth inhibition, especially of the acetoclastic methanogens. Adapted bacteria in anaerobic digestion of swine manure show tolerance up to 1300 mg/l of free ammonia. It has been observed that inhibition at 850 mg/l occurred in thermophilic conditions whereas 800 mg/l has been reported for mesophilic conditions at neutral pH (Björnsson, 2000; Mata-Alverez, 2003). To overcome the problem of ammonia inhibition, two methods are suggested; (a) dilution of digester content with some adequate wastewater and (b) adjustment of feedstock C/N ratio. Both methods rely on the decrease of N concentration.

The carbon/nitrogen (C/N) ratio is also important for process stability. A C/N ratio of 25 to 32 has been reported to have a positive effect on the methane yield. With respect to inhibition, ammonia formation can be neglected only at feedstock with C:N ratios above 20 (Weiland, 1993). At Lower C/N ratios the risk of excess nitrogen not needed for biomass synthesis and therefore becoming inhibitory increases. On the contrary, a very high C/N ratio would lead to N deficiency for biomass synthesis (Ahring, 2003).

- ***Hydrogen sulphide (H_2S).*** Hydrogen sulphide presents a similar behaviour as ammonia and its toxicity is also very much dependent on the environmental conditions of the system, i.e., pH and alkalinity (Mata-Alverez, 2003). H_2S and VFAs are toxic at a pH below 7 (Björnsson, 2000). Total hydrogen sulphide concentrations of 100 to 300 mg/l or free hydrogen sulphide concentrations of 50 to 150 mg/l caused severe inhibition resulting in complete cessation of biogas production. It has been shown that at pH 6, 5% the acetate present is in the protonated or nonionized form which can penetrate the lipid cell membrane (Ahring, 2003).

  The presence of iron ion can also influence these values, as it can remove sulphur anion by precipitation of FeS. Therefore, the presence of metal ions in anaerobic environments can act as either a stimulant or inhibitor. As a reference value, concentrations over 1 mg/l for heavy metals or 5-8 g/l and for metals of group II,

can be toxic according to EPA report and these values are dependent on environmental factors as such care need to be taken when being used.

Retention time. The amount of time that the feed spends in the digester is known as retention time or residence time. The retention time is determined by the average time it takes for organic material to digest as measured by the COD and BOD of the exiting effluent. The longer a substrate is kept under proper reaction conditions, the more complete its degradation will be. The rate of the reaction, however, will decrease with increasing residence time, indicating that there is an optimal time that will achieve the benefits of digestion in a cost effective way. The appropriate time depends on the feedstock, environmental conditions and intended use of the digestate. The retention time for most dry processes ranges between 14 and 30 days and for wet processes it can be as low as 3 days. Ecke (2000), also confirms that in the wet mode, digestate is removed after usually less than ten days solids retention time. Optimal retention time depends on process temperature and the waste composition. It has been reported that volatile suspended solids in a digester could be reduced by 64-85% after only 10 hours, but retention times of 10 days were typical for complete digestion. Reduction in retention time reduces the size of the digester resulting in cost savings.

A shorter retention will lead to a higher gas production rate per reactor volume but a lower overall degradation. Generally, several practices are accepted as aiding in reducing retention time. Two of these are:

Continuous mixing: This approach ensures that bacteria have rapid access to as many digestible surfaces as possible and that environmental characteristics are constant throughout the reactor. E.g. recirculating water and biogas through the digester or employing a stirring blade.

Using low solids: Decreasing solid content is known to reduce retention time both because the bacteria can easily access liquid substrate and because the relevant reactions require water. In addition, at lower solids content, mixing is more complete.

Organic loading rate. The organic loading rate (OLR) determines the volatile solids input to the digester. This parameter has a significant influence on the process performance. It is expressed as the amount of organic matter (as COD or Volatile solids) per reactor volume. A higher OLR will demand more of the bacteria, which may cause the system to crash if it is not prepared. Under feeding the reactor could also lead to reduction in the digester performance due to insufficient nutrients for microbial growth.

4.6.3 Biodegradability and anaerobic digestion

OFMSW consists mainly of the biodegradable fraction, composed of the elements carbon, hydrogen, oxygen and nitrogen. However, in technical applications, not all of the ultimate biodegradable materials are available for anaerobic biodegradation due to many factors (Mata-Alverez, 2003). In accordance with kinetic principles, retention time limits the degree of conversion substrate. Lignin especially requires a longer time for complete decomposition and may be regarded as recalcitrant from the perspective of anaerobic digestion (Ecke, 2000).
Veeken and Hammlers (1999), showed that there is a positive relationship between the hydrolysis rate and the rate of biodegradability. This indicates that the accessibility of the substrate not only increases hydrolysis but also the biodegradability.

Lissens et al. (2001) reported that the origin and kind (composition) of organic solid waste has a significant influence on biodegradability and consequently on biogas yields. For example, mechanically sorted OFMSW has a very different biodegradability compared to source–sorted OFMSW, the latter has a higher digestibility. Effectively, biogas yield in solid waste digestion is much more dependent on waste composition than on process performance.

According to Mata-Alverez (2003), a major part of OFMSW is composed of lignocellulosic organic matter besides small amounts of soluble compounds such as carbohydrates, fats and proteins. Anaerobic biodegradation of organic matter begins with the enzymatic degradation of the solid structure of the substrate as the organic polymers cannot be utilized directly by microorganisms. The rate and the extent of enzymatic degradation depend on the physico-chemical properties of the substrate, the type of microorganisms involved and the environmental conditions.

4.7 Monitoring parameters and reactor stability

There are several parameters that have been used as indicators for process imbalance. An ideal indicator should be easy to measure, should detect the imbalance at an early stage and should reflect the metabolic state of the digester. Also, it is important that the relative change in the indicator should be significant compared to measurement uncertainty and background fluctuations (Poulsen, 2003). Some of the most widely used indicators are described as follows.

4.7.1 Gas production and gas composition

The gas production will initially increase when the reactor is overloaded and then suddenly decrease after a period of time due to accumulation of inhibiting products (acids). Depending on the degree of imbalance, the gas production will decrease while the amount of CO_2 will increase because it is not consumed by H_2 utilizing methanogens. Gas production and composition cannot

be solely used as indicators for process imbalance as changes can simply be a result of changes in the substrate composition. Because low biodegradability of the substrate can lead to low biogas/methane yield and does not necessarily indicate a deficient performance (Poulsen, 2003).

It is therefore important to combine gas production and composition with data for substrate composition and loading. Stenstrom (1983), observed that when overloading of the reactor occurred there was a decline in CH_4 production and consequently an increase in volatile acids concentration. To remedy the situation, feeding rate was temporarily reduced in order to allow the digester to restabilise.

In situations where there have been no changes in substrate composition and loading, a change in gas production and composition can indicate process imbalance. Table 4.3 summarizes some of the most widely used indicators and the principle of their effect (Poulsen, 2003; Ahring, 2003 and Mata-Alverez, 2003).

Table 4.3. Indicator for process imbalance in anaerobic digestion

Indicator	Principle
Gas production	Changes in specific gas production
Gas composition	Changes in the CH_4/CO_2 concentration ratio
pH	Drop in pH due to VFA accumulation
Alkalinity	Detects changes in buffer capacity
Total volatile fatty acids (VFA)	Changes in total concentration of VFA
Individual VFA	Accumulation of individual VFA
COD or volatile solids reduction	Changes in degradation rate

4.7.2 pH, VFA and alkalinity

Process imbalance in an anaerobic digester will normally lead to accumulation of volatile fatty acids (VFA) resulting in a decrease in pH. The increase in acid concentration may not register as a drop in pH immediately if the buffer capacity of the material in the reactor is high. Most organic wastes often have a high content of weak acids and bases resulting in high buffer capacity. But the organic acid level must attain a certain level before it could be detected as a drop in pH. pH is therefore difficult to use as it only reacts slowly to process imbalance (Poulsen, 2003).

pH is easy and inexpensive to measure and it is therefore an effective indicator in systems with low buffer capacity (Mata-Alverez, 2003).

Table 4.4. Possible disturbance of anaerobic digesters and predictable results (Mata- Alverez, 2003).

Disturbance	Arising problem	Final effect if not total digester failure
Flow rate increase	Washout of microorganisms. Methanogens are most affected, given its doubling time	Reduction in: Methane % in gas pH Methane production rate Alkalinity
Feed concentration Increase (overloading)	Imbalances mainly Affecting methanogenic bacteria and resulting in an accumulation of VFAs	Increase in: VFAs Acids different from acetic acid
Introduction of toxic Substances		
Temperature Fluctuations Oxygen exposure		

4.8 Review of established and emerging anaerobic digestion technologies

4.8.1 Single stage systems

In a single stage digester, all the microorganisms coexist in the same reactor and the environmental conditions are kept at equilibrium. These parameters are not necessarily optimal for bacteria, but are acceptable to all. The most crucial parameter is the pH which must always be kept close to neutral in order to ensure the survival of the methanogens. A lower pH than 5.5 in which the acidogens grows well, is detrimental to the methanogens (Ostrem, 2004). In Europe, according to De Baere (2000), about 90% of full-scale plants currently in use for the treatment of OFMSW and biowaste rely on one stage systems, approximately evenly split between “wet” and “dry” operating conditions. The reason for this is probably due to the lower cost of one-stage systems compared to two-stage systems. A complete anaerobic digestion performed in a single reactor, the solids retention time needs to be 20 days (Ecke, 2000).

If anaerobic digestion is to compete with other MSW disposal options, the retention time must be lower than the current standard of 20 days. As already pointed out earlier, the retention time is determined by the average time it takes for organic material to digest completely, as measured by the chemical oxygen demand (COD) of the exiting effluent. Speeding up the process, will make the process more efficient. Microorganisms that consume organic material control the rate of digestion that determines the time for which the substrate must remain in the digestion chamber, and therefore the size and cost of the digester.

Individual bacteria cannot be made to digest material quickly, however there are several ways to achieve a shorter retention time. Physical separation of the hydrolytic-acidification and acetogenic-methanogenic phases of the overall anaerobic digestion process according to Dinamarca et al. (2003) and Ghosh et al. (2000), provides a hospitable environment for the separate phases and allow the bacteria to reproduce easier, giving them a greater working population. Separate acid and methane phase fermentations have shown an improved anaerobic digestion system performance relative to that of a single-stage, high-rate digestion (Ghosh et al., 2000).

Digestion at high and low solids. Digestion can be practiced in two broad categories of solid content: high-solids (dry) digestion, with typical dry solids content of 25-30%, and low-solids (wet) digestion with dry solids content of less than 15%. A higher solid content leads to smaller and therefore cheaper reactors. However, more costly pumps and higher wear and tear on the machinery to move denser material (increased maintenance costs) may offset this price savings. According to Lechner (2005), reported that one major disadvantage is that the mixing, which is carried out by agitators or pistons pumps are energy-intensive and also, when transient dry matter content in the fermenter approaches 40%, there is a danger of agitator lock and stoppage of material transport.

Systems with lower solids usually have better mixing and higher degree of digestion. On the other hand, wet digestion requires a higher energy input because there is more substrate to be heated in bigger reactors. For many waste streams, large quantities of water must be added to reduce the solids content, thereby adding to the additional cost of dewatering the sludge to reuse process water (Ostrem, 2004).

Lechner (2005), further pointed out that, regarding the eminent desired high output per unit volume and per unit time, dry fermentation seems to offer distinct advantages over wet processes. Due to its low water content, high concentration of biologically decomposable organic material (the material basis of fermentation process) is present.

4.8.2 Double-Stage systems

Generally, two stages are employed where the first stage constitutes the liquefaction-acidification compartment, with a rate limited by difficult anaerobically degradable substrates such as the hydrolysis of lignocellulose complexes. The second stage constitutes the acetogenic and methanogenic compartment, with rate limited by the slow microbial growth rate of the methanogenic bacteria (Mata-Alverez, 2003). Two stage variations according to Björnsson (2000), Mata-Alverez (2003), and Ahring (2003), are shown in figure 4.7.

The two-stage approach has successfully been applied in several cases. One important application is when the substrate is in a solid form and the first phase includes both liquefaction and acidification (A) while the later (B), the first phase involves liquid form of substrate.

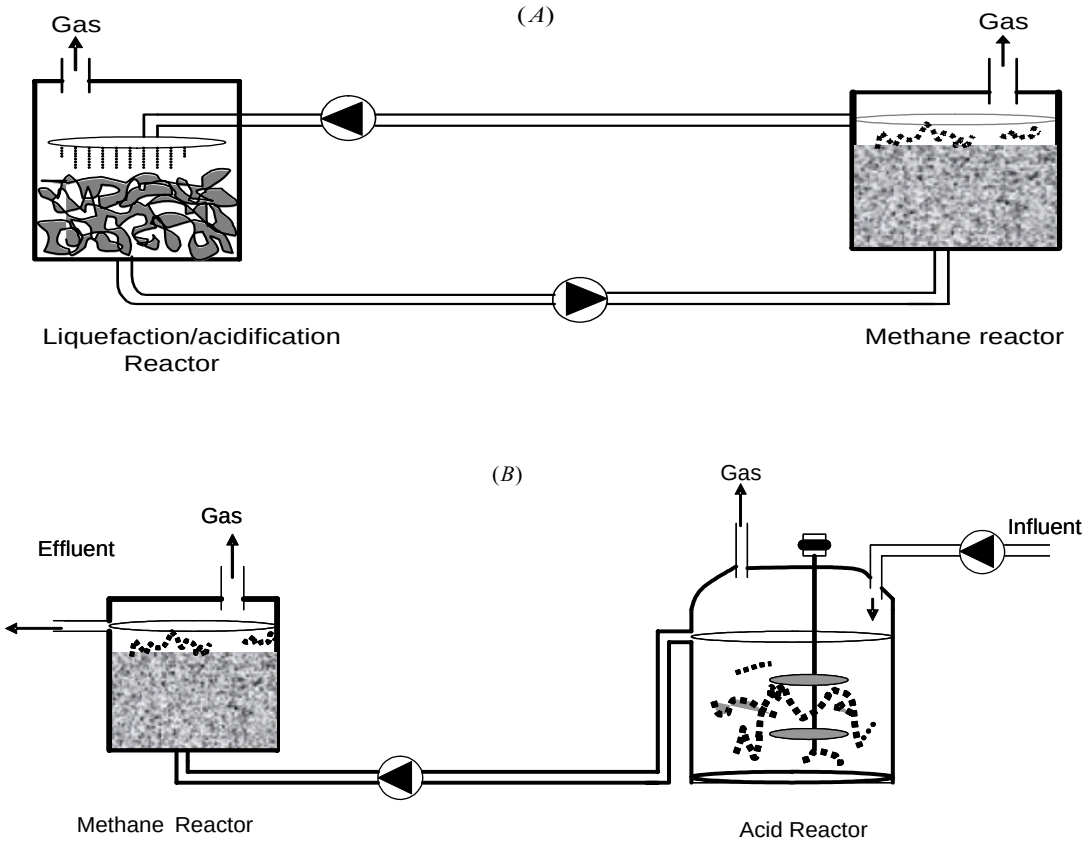


Figure 4.7. Variation in the two phase approach (A and B).

In order to increase rates and resistance to shock loads or inhibiting substances, it is desirable to achieve high cell densities of the methanogenic bacteria. To achieve this it is essential to increase the rate of methanogenesis by designing the second reactor with a biomass retention scheme as described earlier. The main advantage of a two-stage system is not its higher biogas yield or rate but rather its increased biological stability for wastes which cause unstable performance in one-stage systems (i.e. cellulose – poor wastes with C/N ratios lower than 10) (Lissens et al., 2001 and Cha et al., 1997). It is important to define the treatment objectives first in order to compare the different anaerobic treatment systems. This will largely depend on the local situation at the treatment site and the possibilities for effluent reuse. Nevertheless, the system chosen should offer the highest possible organic load removal efficiency at the shortest possible Hydraulic Retention Time (HRT) (Ostrem, 2004).

Enhanced biomass retention. The low specific growth rates of some of the bacteria involved in anaerobic digestion process is the main limitations. As a result, long retention times are required to avoid washout of active biomass in conventional, continuously stirred tank reactors (CSTRs). Biomass retention can be achieved by uncoupling the hydraulic and solids retention time thereby ensuring high solid content in the methanogenic reactor.

A possibility to achieve higher capacity and increased stability is to retain the slow growing microorganisms within the process. This can be accomplished by recirculation of sedimented sludge, or by using a process configuration that allows the formation of granulated sludge of high density, which is retained inside the reactor. The third approach is by the use of support material to retain the slow-growing microorganisms in a biofilm (Bjornsson, 2000; Ahring, 2003 and Mata-Alverez, 2003). The unique biomass formation makes it possible for the processes to withstand high concentrations of otherwise inhibitory compounds (Ahring, 2003). Figure 4.8 illustrates some of the most commonly used process configurations for biomass retention (Bjornsson, 2000 and Ahring, 2003).

The two basic reactor types are the anaerobic filters (B) and the fluidized bed reactors (C). Both take advantage of the microbial tendency to stick to surfaces.

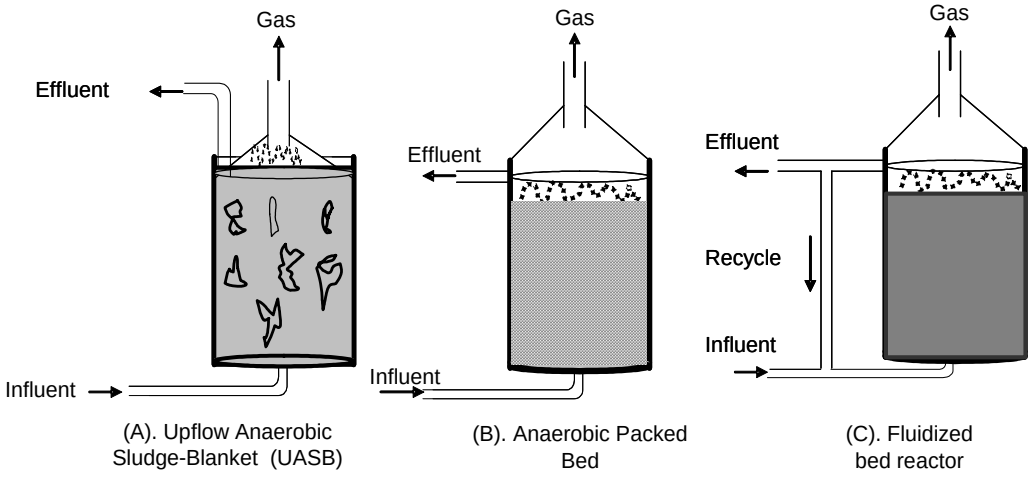


Figure 4.8. Some of the most commonly used configurations for biomass retention.

In the first case, microorganisms are attached to a fixed, porous and inert support matrix of e.g. stones, plastic or unglazed porcelain; in the later they grow on suspended bed material out of rock, gravel or sand. Reactor (A) according to Rijkens et al. (1984) emerged from both anaerobic filters and fluidized bed reactors called Upflow Anaerobic Sludge-Blanket (UASB) reactor. The influent is fed at the bottom and passes a sludge blanket of biologically formed granules. Biogas formed during treatment sticks to some of the particles and lifts them up to the top of the reactor (Lettinga et al., 1997).

Presently, a new type of UASB reactor called Biobed® EGSB (Expanded Granular Sludge Bed) reactor has been invented. It is a combination of the fluidized bed and the UASB technology, developed for high fluid and gas velocities (Ecke, 2000).

Examples of commercial plants with biomass retention scheme include the BTA (Biotechnische Abfallverwertung GMbh & Co) and the Biopercolat:

- ✓ In the BTA wet-wet process, pretreatment is centered on a hydro-pulper, which receives the source-sorted waste from a screw-mill, opens bags and disintegrates larger agglomerated particles. In the hydro-pulper, the waste is mixed with recirculated process water and the organic is dissolved through intense agitation (Ahring, 2003; Kübler et al., 1992). The pulp which is 10% TS is pasteurized and dewatered. The liquor is sent directly to the methanogenic reactor. The methanogenic reactor receiving only liquid is designed as a fixed film loop reactor to increase biomass concentration and age.
- ✓ The Biopercolat follows the same principles as the BTA process. The only difference is that in the Biopercolat the first stage is carried out under 'dry' and microaerophilic conditions where it is continuously percolated with process water to accelerate the liquefaction reaction. The process water containing up to 100 g COD/l, is fed to an anaerobic plug flow filter filled with a support material. The advantage of this design include the separate optimization of the first stage, through aeration, and the second stage, through attached growth, and allows the system to run at exceedingly low overall retention time of 7 days. The Biopercolat system is quite innovative from a technical point of view (Lissen, 2001 and Mata-Alverez, 2003).

Other commercial designs without biomass retention scheme include the 'wet-wet' or 'dry-dry' Schwarting Uhde and BRV processes (Lissen et al., 2001 and Kübler et al., 1992).

Ghosh (1991), observed that the most important advantage is the fact that the methanogens in the second phase could be effectively protected by monitoring closely the effluent reaching the methanogens from the acidogenic phase.

This allows potential problems to be eliminated before the process liquid reaches the sensitive methanogens. Two–phase anaerobic system according to Wang et al. (2002) is also suitable for organic wastewater treatment with high concentrations of organic suspended solids.

4.9 Batch systems

In the batch process, the feedstock is fed to the digester at the start of the degradation period and sealed for the duration of digestion. All the stages occur more or less consecutively and therefore

the production of biogas follows a bell curve. There are three types of batch systems – single stage batch system, sequential batch system and an Upflow Anaerobic Sludge Blanket reactor.

The single-stage batch system involves re-circulating the leachate to the top of the same reactor. An example of such a system is the Biocel process in Lelystad, The Netherlands. The waste fed to these unstirred is pre-mixed with inoculum. The leachates are collected in chambers under the reactors and recycled to the top of each reactor. The waste is kept within the reactor for several days, until biogas production stops.

The sequential batch process comprises two or more reactors. The leachate from the first reactor, containing a high level of organic acids, is re-circulated to the second reactor where methanogenesis occurs. The leachate of the methanogenic reactor, containing little or no acid, is combined with pH buffering agents and recirculated to the first reactor. This guarantees inoculation between the two reactors.

The third type of batch process is the hybrid batch-UASB process, which is very similar to the multi-stage process with two reactors. The first reactor is simple batch reactor but the second methanogenic reactor is an upflow anaerobic sludge blanket (UASB) reactor (Vandervivere et al., 2002; Verma, 2002).

Lissens et al. (2001) reported that the batch systems have the simplest designs and are the least expensive solid waste digesters, and have high potential for application in the developing countries. Also, it has retention time ranging from 30-60 days and only about 1/3 of the tank volume is used for active digestion. For this type of system, the main disadvantages are the large tank volume required due to the long retention time, organic loading rate and the formation of a scum layer (Ostrem, 2004).

4.10 Summary of advantages and disadvantages of reactor types

Table 4.5 summarises the pros and cons of the various systems reported by Björnsson, 2000; Ecke, (2000); Mata-Alverez, (2003) and Ghosh et al, (2000).

Table 4.5. Advantages and disadvantages of reactor types

Criteria	Advantages	Disadvantages
Wet Single Stage		
Technical	Inspired from known process.	Short-circuiting Sink and float phases Abrasion with sand/grit Complicated pre-treatment
Environmental	Dilution of inhibitors with fresh water.	Particularly sensitive to shock loads as inhibitors spread immediately in reactor.

		Where pre-sorting is required, VS is lost with inert
Economic and Environmental	Equipment to handle slurries are cheaper.	High consumption of water Additional pretreatment of steps Larger reactor volume (because of dilution) High energy requirement for heating large volumes
Dry Single Stage		
Technical	No moving parts inside reactor (maintenance less difficult). Robust (inerts and plastics) need not be removed). No short-circuiting	Wet wastes (< 20% TS) cannot be treated
Environmental	Low VS loss in pretreatment Large OLR (high biomass) Limited dispersion of transient peak concentrations of inhibitors (these are constrained)	Little possibility to dilute inhibitors
Economic and Environmental	Cheaper pretreatment and smaller reactors Complete hygienisation Low water usage Low heat requirement (No water to heat up)	Though more robust, is more expensive
Two-Stage processes		
Technical	Design flexibility	
Environmental	More reliable for cellulose kitchen waste Only reliable design (with biomass retention) for wastes with C/N ratios <20	Smaller biogas yields (when solids not methanogenized)
Economic and Environmental	Less heavy metal in compost (when solids not methanogenized	Larger investment
Batch systems		
Technical	Simple Low tech Robust (inerts, plastics	Clogging Need for bulking agent Risk of explosion during empting of reactor

	need not be removed)	
Environmental	Reliable process due to niches and use of several reactors	Poor biogas yield due to channeling of percolate Small OLR
Economic and Environmental	Cheap Low water consumption	Large Land requirement (similar to aerobic processes)

4.11 Process enhancement and shortening of digestion time

Due to the economic constraints in most of the African countries, the development of an efficient anaerobic digestion system comprising of a simple design and less capital cost is very important. In this regard, a review of the anaerobic digestion process optimization and factors that affect the stability of the process is considered. In an effort to optimize and shorten the overall process time, it means individual subsystems need to be provided with the optimum conditions to establish the economy of the technology. Brief descriptions of the factors that need to be considered to enhance the various stages are presented.

4.11.1 Hydrolysis stage

The major part of organic fraction of MSW that are fed into reactors contains a large fraction of suspended solids and complex soluble matter. The main biodegradable components include carbohydrate, lipids and proteins (Mata-Alverez, 2003). In anaerobic treatment of organic wastes, which consist generally of dissolved and particulate components, solids hydrolysis is the rate-limiting step of the whole anaerobic degradation (Palmowski and Müller, 2003).

To support the hydrolysis and improve the entire degradation, the following steps must be taken to ensure that, microaerophilic process in the hydrolysis hastens liquefaction compared to anaerobic conditions. In the BRV process, micro aerobic process was employed at the hydrolysis-stage which resulted in fast liquefaction compared to under anaerobic conditions. The extent of liquefaction was high enough to compensate for COD losses due to respiration (Palmowski and Müller, 2003).

Dilution of the waste. According to Lechner (2005), moisture content is of considerable importance because water.

- Constitutes a fundamental building block of living microorganisms by influencing the structure and properties of essential biomolecules and cell components;
- Serves as transport medium for material supply and removal in cellular material exchange; and
- Is essential for microbial exchange mechanisms to take place.

Therefore, an appropriate dilution of water (low solids) ensures better mixing, greater access to substrate and higher degree of digestion (Ostrem, 2004). Stroot et al, (2001) observed that, as a whole pulping of the solid waste results in a better hydrolysis and homogenization of the waste. Convection currents ensures an even temperature distribution in the reactor (Ostrem, 2004).

Leachate recirculation. Intermittent leachate recirculation help flush out solubilized products and periodic leachate removal with water replacement increases the buffer system thereby enhancing the hydrolysis of organic material. The experiments and simulation of Veeken and Hamelers (2000), on the solid state digestion of biowaste in batch reactors showed that the reactor performance could be improved by applying leachate recirculation. Leachate recycling increases the digestion rate by means of increasing moisture moving through the digestion system and accelerating the stabilization of waste (Wang et al., 2003).

Anaerobic treatment process with recirculation of process water from effluent from the methane to the hydrolysis requires additional control precaution because of the risk of enrichment with salts, nitrogen compounds and volatile fatty acids. The respective compounds can be removed by diluting or purging the process water before an inhibitory concentration is reached. In comparison to other reactor types, percolation processes are less sensitive to contaminants and foreign substances (Ecke, 2000).

Size reduction. Veeken and Hammelers (1999), reported that the rate of hydrolysis of particulate organic matter is determined by the adsorption of hydrolytic enzymes to the biodegradable surface sites and leads to increase in biodegradability. Thus, pre-processing the waste will make it more easily degradable requiring fewer bacteria, allowing the microorganisms to proceed to the final stages of digestion in less time. Palmowski and Müller (2003), observed two positive effects of communition of fibre material that are particularly resistant to hydrolysis. A significant improvement of the degree of degradation was observed after communition. Further, it is observed that degradation rate of communited samples were significantly higher than uncommunited samples. Sanders et al. (2000) observed that the rate of hydrolysis was directly related to the amount of substrate surface available and that surface of the particulate substrate was a key factor in the hydrolysis process.

4.11.2 The methanogenic stage

All types of two-stage system, regardless of whether biomass is accumulated or not, provides some protection against the fluctuation of organic loading rate. Furthermore, it was noticed that only two-stage systems with biomass retention schemes display stable performance with wastes greatly charged with nitrogen or other inhibitors (Mata-Alverez, 2003). This means that a

substance is provided on which the microorganism can live inside the reactor preventing a greater number from being washed out, thereby establishing a more stable working population. Some of the most promising research has shown retention times in the range of 2-5 days, but this is for very dilute, low solids waste (Ostrem, 2004).

4.11.3 Feedstock pretreatment processes

In anaerobic digestion, pretreatment is considered as the first phase of the overall process. Van Lier et al. (2001) reported that enhancement of the biodegradability of particulate substrate is mainly based on a better accessibility of the substrate for the enzymes. The main objective of pretreatment is to accelerate the digestion of solid waste to raise the degree of degradation and thus to decrease the amount of digestate to be disposed of and the digestion time. In addition, Palmowski et al. (2000) explained that size reduction provides uniform small particle size of the substrate with an enlarged available surface that can support the biological process in two ways, i.e., improved reactor gas production and reduction in the technical digestion time. Also, the other advantage is the harmonization of the digestion time in case of heterogeneous substrate material and the reduction of the required reactor volume. There are several ways to accomplish this.

- ✓ **Mechanical pretreatment.** This process involves the segregation of inert and bulky materials from the organic fraction which is then followed by particle size reduction (Hansen et al., 2003). These have positive effects on the anaerobic biodegradability of the substrate through an increase of available specific surface to the medium. For a tomato waste chopped to particle sizes of 1.3 to 20 mm, it was realized that the biogas production rate and solid reduction are inversely proportional to the substrate's average particle diameter (Hills et al., 1984). Results have shown that both biogas production and reduction of the technical digestion time were increased by communition for all substrates especially for those of low biodegradability like leaves, seeds and hay stems (Palmowski et al., 2000).
- ✓ **Chemical methods.** This process involves the destruction of complex organic compound by means of strong mineral acids, alkali or ozone. For example, application of alkali such as sodium hydroxide results in the rupture of lignin, and increase in surface area due to cellulose swelling, and some degree of decrystallization of cellulose. The effectiveness of this pretreatment has been demonstrated with an increased enzymatic digestibility and enhanced digestibility. Pretreatment of wheat straw with sodium hydroxide at ambient temperature resulted in an improvement of the anaerobic biodegradability of the material. The disadvantage of these two processes is that, large amount of chemicals are required

and this cause in general, strong increase of the mineral content of the sludge liquid (Pavlostathis et al., 1985). Ozone treatment is the most interesting chemical pretreatment method. It causes a hydrolysis and solubilization of cell walls resulting in release of biodegradable cell material. Biogas production can be doubled in comparism with untreated sludge. A main disadvantage of the use of ozone is that the dewatering properties of the sludge generally deteriorate (Lens et al., 2004).

- ✓ **Enzymatic and microbial pretreatment**. This is the addition of hydrolytic enzymes as a pretreatment designed to increase the yield and the rate of particulate matter solubilization during anaerobic digestion of the solid waste, particularly waste water sludge or cellulose-rich materials (Mata-Alverez, 2003). It is important to mention that the costs of the use of enzymes are generally high, while the effect on biogas production is very limited (Lens et al., 2004). For the hydrolysis of OFMSW, the amount of hydrolytic enzymes is adequate and not rate-limiting for hydrolysis. This is expected since the growth rate of both the hydrolytic and the fermentative bacteria are very fast (Mata-Alverez, 2003).
- ✓ **Thermal pretreatment**. This is usually used as a conditioning process for raw or digested sludges; thermal hydrolysis allows a complete energy recovery from organic waste and complete disinfection of the waste (Schieder et al., 2000). The main disadvantage is the high investment cost. However, the advantages are, there is a strong reduction of the amount of volatile solids, reduction in hydraulic retention and improvement of the mechanical dewaterability of the substrate after digestion resulting in a lower volume of sludge (Lens et al., 2004 and Mata-Alverez, 2003).
- ✓ **Other physical pretreatment option** for lignocellulosic materials includes; Steam explosion and irradiation. Steam explosion process involves pressurizing woody substrates with steam at temperatures of 130-180^{o}C for a period of 30 min and then suddenly releasing it to the atmospheric pressure thereby shattering the structure. Irradiation pretreatment is carried out by subjecting the woody material to gamma rays or high-velocity electrons which substantially improves the digestibility of these materials by rumen microorganisms.

4.11.4 Mixing

The manner in which substrate flow through the reactor impacts the degree of contact the substrate has with the resident bacteria and therefore how quickly it is digested. Also feeding technique greatly affect the mixing ability of the digesters (Stenstrom et al., 1983). In small

conventional systems such as covered lagoons, the feedstock is fed and allowed to biodegrade without mixing.

But in recent systems, improvement have been made by changing the manner in which materials flow through the reactor such as in complete mix digesters and plug flow reactors or in the way, in which materials are mixed for example, through agitation, gas injection, or recirculation. Other possibilities that exist include;

- Mixing taking place along the pathway the waste travels before it is removed
- Systems having interior walls in a cylindrical chamber which requires greater distance traveled by the waste thereby increasing mixing.

Mechanical mixers inside the tanks are less common because maintenance is extremely difficult in that, for sealed tanks, the system must be shut down before interior machinery can be accessed. Mixing can also be achieved through recirculation of waste or process water. For the former, after digestate is removed from the reactor at the end of its retention time, a percentage of it is fed into the stream of incoming fresh waste. This serves to inoculate the fresh waste with bacteria and increase movement in the reactor. In the case of the latter, part of the leachate liquid is intermittently recycled back on to the waste bed which ensures mixing. Excessive mixing can disrupt microbes therefore it is essential that optimum care is taken during mixing (Ostrem, 2000).

4.12 Summary

Chapter two and three outline the problems associated with solid waste management in developing countries (e.g. Accra, Ghana) thus justifying the need for pretreatment before landfilling. Chapter four exclusively covers the anaerobic digestion process, reactor types and their applications. The essential points highlighted in chapter four.are:

- When digesting highly biodegradable wastes, such as source sorted OFMSW or fruit and vegetable wastes, it is advisable to use a two-phase anaerobic digestion system as this option allows much higher loads in the digester and is more flexible.
- Success has been achieved with the anaerobic digestion of solid waste at ambient temperature, which is known to be cost effective and suitable for developing countries;
- And thirdly, it was observed that mixing which is carried out by agitators or pistons pumps are energy-intensive and also, when transient dry matter content in

the fermenter approaches 40%, there is a danger of agitator lock and stoppage of material transport.

In the next chapter, the methodology employed which follows a laboratory-scale investigation into pretreatment of UMSW is presented.

5 EXPERIMENTAL

5.1 Introduction

Two main objectives form the basis on which the experimental plan design was made; i.e., (i) to achieve optimal biogas production and (ii) at a reduced retention time. Based on this, the following research questions were raised and adequately answered.

5.2 Research question

What extent of biodegradation is achievable through anaerobic digestion of UMSW? And consequently, what does it involve in practice to realise it? Based on review of the literature and on known experimental results, a laboratory study was designed to test a number of hypotheses to adequately answer these questions.

Hypotheses

1. It has been observed that appropriate water flow rate (dilution) with water usually has better mixing, greater access to substrate and higher degree of digestion (Hofenk, 1985 and Ostrem, 2004). Therefore, what flow rate (dilution) would result in optimal degradation?

   Dilution process is related to a an important process parameter called hydraulic retention time (HRT) which is defined as the ratio of the reactor volume to input volumetric flow rate as shown in equation 5.1, and this controls the degree of digestion. It measures the time that a fluid element spends inside the reactor.

$$HRT = \frac{V}{Q} \qquad 5.1$$

$$\Rightarrow$$

$$HRT\ \alpha\ \frac{1}{Q} \qquad 5.2$$

   Where V is the reactor volume (m^3) and Q the water flow rate (m^3/day).

   High delivery of liquid (short HRT) will result in short contact time between the bacteria and the substrate, thus organic material will not be fully degraded resulting in low biogas yield and possible microbial wash out.

   Low delivery of liquid (high HRT) will ensure long contact time between the bacteria and the organic substrate resulting in high substrate degradation especially in the case of the methane reactor but longer digestion time. In addition, long contact time could affect the hydrolytic bacteria if the pH is too low, i.e. inhibition effect. The efficiency not only depends on the HRT, but also the feedstock composition and reactor temperature.

The cumulative leached COD from the degradation of a particulate matter is dependent partly on the water flow rate and for that matter the HRT. The cumulative COD production according to Veeken et al. (2000) is known to obey the first order kinetics as shown in equation 4.23.

$$C = C_o\left(1 - \exp\left(-k_H \cdot t\right)\right) \qquad 5.3$$

Where C is the cumulative COD production (g/l); C_o is the starting COD concentration of the substrate (g/l); K_H is the hydrolysis rate constant (d^{-1}) and t is the time (d). This function is a pure empirical expression that reflects the cumulative effect of many processes and has been realised that the hydrolysis rate is proportional to the substrate volatile solids and inversely proportional to the VFA concentration.

The leached COD is dependent on the water flow rate regime and as well many other factors. Also, the cumulative leached COD is a positive indication for hydrolysis rate which is reflected in a determinable parameter, the hydrolysis rate constant (K_H). Therefore, the measurement of fermentation product (e.g. COD) the hydrolysis rate constant can be calculated.

Also, the specific methane production (SMP) is inversely related to the HRT as shown in equation 4.28 reported by Mace et al. (2003).

$$SMP = B_o / (1 + 1/(k \cdot HRT) \qquad 5.4$$

Where *SMP* is the specific methane potential (m^3/kg VS), *Bo* is the ultimate methane potential and *K* is the hydrolysis rate constant (d^{-1}).

2. It has also been observed that with high rate double stage digesters, digestion time could be reduced to 14 and 30 days for dry processes and for wet processes it can be as low as 3 days for biowastes. However, a retention time of 10 days is typical for complete digestion of biowaste (Ecke et al., 2000). Therefore, to what extent of biodegradation is achievable at 7, 10 and 14 days retention times?
3. One of the aims of the experimental design was to perform the anaerobic digestion process of the solid waste under mesophilic conditions (30^oC). However, in the tropical countries ambient temperatures could be sufficient for the digestion process. Therefore, to what extent of biodegradation is achievable at ambient temperature, 30 ^oC and 35 ^oC.
4. Veeken and Hammelers. (1999) observed that hydrolysis rate is directly related to the amount of substrate surface available and the microorganisms and also that the rate of hydrolysis of particulate organic matter is determined by the adsorption of hydrolytic enzymes to the biodegradable surface sites and this leads to increase in biodegradability. Thus size reduction of the waste will make it more easily degradable requiring fewer

bacteria, allowing them to proceed to the final stages of digestion in less time. Therefore, to what extent of biodegradation is achievable through anaerobic digestion of pre-processed substrates (shredded, source sorted and mechanical sorted wastes).

Before the first set of experiments were carried out, it was crucial to carry out start-up phase experiment of the methane reactor to adapt the microorganisms to the substrate in question.

The waste to be digested was dry (21-26% TS), and digesting it in its original form would involve time and also limit organic substrate removal based on the physical nature (with impurities > 40 mm) of the waste, hence there was the need for dilution of the waste with water.

After the start-up phase, initial sets of experiments were designed to determine the appropriate dilution water flow rate regimes (1-1.75 liters of water/kg input waste. day) and a variable stepwise decrease of water flow rate regimes (1-1.5 litres of water/kg input waste. day) which differed fundamentally in the Hydraulic Retention Time (HRT), on leaching of the organic fraction from the matrix of unsorted waste resulting in the production of chemical and biological oxygen demand (COD and BOD), organic acid (OA), pH and the overall reduction of the waste volume at the end. Similarly to the case of the hydrolysis, the same flow rate regimes of COD laden leached liquid were allowed into the methane reactor resulting in various gas production rates.

Secondly, influence of solid retention time (7, 10 and 14 days) on the extent of leaching as COD, and OA and gas production rate at a predetermined water flow rate regime (1.25 litres water/kg input waste. day) with similar leached liquid flow rate regimes into the methane reactor was studied.

Thirdly, the influence of temperature (at room temp, 30 and 35 ^{o}C) on the extent of leaching (as COD, BOD_5 and OA) and gas production rate at a predetermined dilution water flow rate (1.25 litres water/kg input waste. day) was carried out.

The fourth sets of experiment was carried out to study the influence of pretreatment of input material through mechanical sorting (8-40 mm, 40-120 mm), source sorted waste (fruit and vegetable), and control sample of an unsorted waste on leaching and biogas production.

Finally, preliminary fermentation was carried out in a single stage digester using UMSW as input material at a water dilution of (1.75 litres water/kg input waste) on leaching of COD, OA, pH and subsequent biogas production. Table 5.1 summarizes the various experiments performed to determine the biomethanization behaviour of the simulated UMSW under the influence of number of factors on the process performance of the double stage anaerobic digester described in figure 5.2.

Table 5.1. Description of the main laboratory scale experiments and its operational conditions.

Experiments	Description of the main parameter tested	Liq. Flow rate (l/ kg * d) in H_R	Av. HRT (d) H_R	Av. HRT (d) M_R	Temp(^oC) H_R/M_R	No. of runs
Expt 5.6.1	Slurry bed inoculation	Varied	Varied	Varied	30/38±2	1
Expt 5.6.2	Influence of water flow rate on solubilization of particulate matter	Varied	Varied	Varied	30/38±2	14
Expt 5.6.3	Degradation at different solid retention times	1,25	0.49	4	30/38±2	6
Expt 5.6.4	Influence of temperature on the rate of degradation	1,25	0.49	4	Varied	6
Expt 5.6.5	Pre-processed substrate and their effect on hydrolysis	1,25	0.49	4	30/38±2	16
Expt 5.6.6	Single stage fermentation	1,75	2,9		35±2	2

* Av.HRT represent average hydraulic retention times in the hydrolysis (H_R) and methane (M_R) reactor respectively. Each experiment was run in duplicate.

Liquid flow rate or dilution water in this case, is expressed as *liters of liquid/kg input material/day* which shows the quantity of dilution water applied to the input waste during hydrolysis for each experiment. It is calculated according to the equation (5.4).

$$Flow\,rate\;\; Fr\left(l/kg*d\right)=\left(\frac{Litres\;of\;\;liquid\;\;allowed\;\text{into the hydrolysis reactor}}{(ki\log ram\;of\;\;input\;\;waste\;\text{into hydrolysis reactor})*day}\right) \qquad 5.5$$

5.3 Materials and methods

5.3.1 Solid waste acquisition and preparation

The waste composition in Germany or most developed countries has less organic or degradable fraction (45-56 %) than those observed in developing countries which are often greater than 65%. Using the waste composition in Germany for the research would not reflect the real situation found in Ghana or other developing countries. Therefore, there was a need for a "derived sample" referring to a simulated waste as a representative material found in developing countries. Simulated input waste was prepared by remixing the various unsorted solid waste components and market waste in proportions by weight corresponding to their respective amounts as they occur in reality, i.e., organic fraction > 65%. (See figure 5.1 and mass balance equations 5.6-5.10 for the derivation of the simulated waste model). The characteristics of the simulated waste were developed based on the waste composition of Accra, the capital city of Ghana (Table 5.2).

Unsorted municipal solid waste (UMSW) was collected (grab sample) from the landfill in Cottbus (Saspow). Unsorted household waste meant for practical analysis in the laboratory was also sometimes used. A mixture of vegetable and fruit waste used to blend the unsorted waste

was collected biweekly from a wholesale supermarket in Cottbus. The market waste was hand-sorted in order to eliminate packaging materials and then chopped to about 2-5 cm in diameter size pieces before blending.

Blending: The simulated input material was finally prepared by blending 50 parts-by-weight of the unsorted municipal solid waste fraction and 50 parts-by-weight of the market waste. Figure 5.1 shows the scheme of the blend.

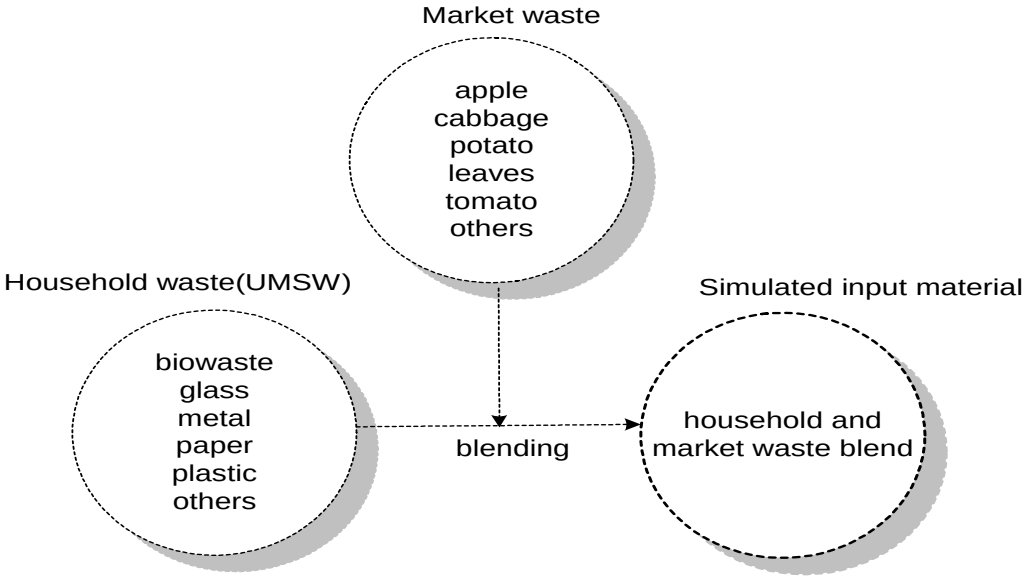


Figure 5.1. A model of the simulated input material for the experiments

The individual compositions were derived from the mass and component balances shown in equation 5.6-5.10.

Overall total mass balance

$$Mass_{household\ \ waste} + Mass_{market\ \ waste} = Mass_{final\ \ input\ \ material} \qquad 5.6$$

Mass balance of household waste and market waste

$$Mass_{Simulated\ \ market\ \ waste} = \sum_{i=apple}^{others} Mass_i = {Mass_{input\ \ material}}/{2} \qquad 5.7$$

$$Mass_{Simulated\ \ Unsorted\ \ household\ \ waste} = \sum_{i=biowaste}^{others} Mass_i = {Mass_{input\ \ material}}/{2} \qquad 5.8$$

Component balance

e.g:

$$Mass_{Simulated\ \ glass} = 2 * \left(\%\, Mass_{glass} * Mass_{Simulated\ \ Unsorted\ \ household\ \ waste}\right) \qquad 5.9$$

$$Mass_{Simulated\ Org.Fraction} = Mass_{Simulated\ biowaste} + Mass_{Market\ waste} \qquad 5.10$$

The basic characteristics of the "simulated waste" used in the study which reflects the average percentage values of the different materials present in the waste composition of Accra, Ghana is shown below (table 5.2).

Table 5.2. Simulated and real waste characteristics of Accra

On the basis of 20 kg (dry wt) input simulated material used for the study			Composition of solid waste (by wt) in Accra metropolis (AMA, 2002)	
Composition of simulated input material	Mass (kg)	Mass %	Composition	Mass %
Organic fraction	13,00	65,0	Organic fraction	65,0
Paper	1,20	6,0	Paper	6,0
Plastic	0,70	3,5	Plastic	3,5
Glass	0,60	3,0	Glass	3,0
Metal	0,50	2,5	Metal	2,5
Textiles	0,34	1,7	Textiles	1,7
Inert material	3,42	17,1	Inert material	17,1
Others	0,24	1,2	Others	1,2
Total	20	100	Total	100

The fruit and the vegetable waste was chopped to an average size of about 2-5 cm in diameter, and then mixed with the unsorted waste based on the mass balance information presented above. As observed, the chopped fruit and vegetable was highly wet material (88±8% moisture content) and appeared to be highly biodegradable.

In order to avoid degradation at ambient temperature of the remaining wastes meant for subsequent experiments, it was then loosely packed in a 60 and 120 litre polypropylene barrels with an air tight lids and stored in a laboratory cool chamber at a temperature of about +3^{o}C.

5.3.2 Laboratory-scale reactor set-up

Background of reactor design. Previous studies according to Wang et al. (2003) have demonstrated that:

I. Leachate recycling increases the digestion rate by means of increasing moisture moving through the digestion system and accelerating the stabilization of waste
II. Separating anaerobic process into two phases, i.e., acidification and methanogenesis phases facilitates the optimal growth for non-methanogenic and methanogenic bacteria.

III. Interactions between the two stage reactors by the recirculation of treated liquid would lead to the improvement of pH buffering capacity of the acid phase digestion.

Based on these considerations, a two-stage percolating bioreactor (figure 5.2) was tested using unsorted municipal solid waste.

Optimization design conditions employed in the study. The two-stage digester design performing at mesophilic conditions (30 ±2^{o}C)was used where the anaerobic process was separated into two phases, i.e., hydrolysis and acidification in one reactor and methanogenesis in the other to facilitate the optimal growth for non-methanogenic and methanogenic bacteria. The separate optimization designs employed in the study were;

Hydrolysis stage.

- ✓ Micro aerophilic conditions in the digester to facilitate the rate of liquefaction.
- ✓ Leachate recycling to increase the digestion rate by means of increasing moisture moving through the digester system.
- ✓ Percolation process enhances leaching of soluble particulate matter and it is known to be less sensitive to contaminants and foreign substances.

Methanogenic stage.

- ✓ Slurry bed digester with biomass retention
- ✓ Intermittent delivery of hydrolysed liquid and Stirring of the reactor

***Treatment approach*:** This process is a percolating one, where a continuous wetting of the waste bed with fresh water or effluent from the methane reactor, aimed at percolating/leaching out into solution of hydrolyzed materials. A part of the leached contents of the hydrolysis reactor is periodically recycled through solid/liquid separation. Acidified products are removed with the liquid phase. Intermittent re-suspending of the solids in the hydrolytic reactor with the methane reactor effluent helps to keep the volatile fatty acid level in check and also increases the buffer capacity in the hydrolysis reactor. Accumulated part of the content of hydrolytic reactor is stored in a buffer tank and intermittently pumped into a specific methane reactor containing a slurry bed, which treats effectively the COD laden leachate while producing biogas. The output of the hydrolysis reactor is finally dewatered. The non-degraded materials with total solids (TS) content of 35-40% are discarded in a university campus bin. In section 5.3.3, the description of the reactor set-up is presented.

5.3.3 Description of the laboratory-scale reactor set-up

The configuration of the two-stage system consisting of (i) a hydrolyser and, (ii) methanogenic reactors (figure 5.2), where the two key steps of anaerobic digestion process took place is described below.

Hydrolysis phase. A percolating microaerophilic (Low oxygen concentration) hydrolytic reactor design was employed in the study. These reactors are polyethylene barrels (H_{R1} and H_{R2}) with a volume capacity of 120 litres with effective volume of 12 litres. The designated volume available for the waste compaction is about 75 to 80 litres. The upper 10-15 litres of the reactor volume is left to provide allowable space for the sprayer or sprinkler in order to distribute uniformly the process water or recirculated leachate into the waste bed. These barrels are airtight and insulated with styrene sheet and binded by cello tape.

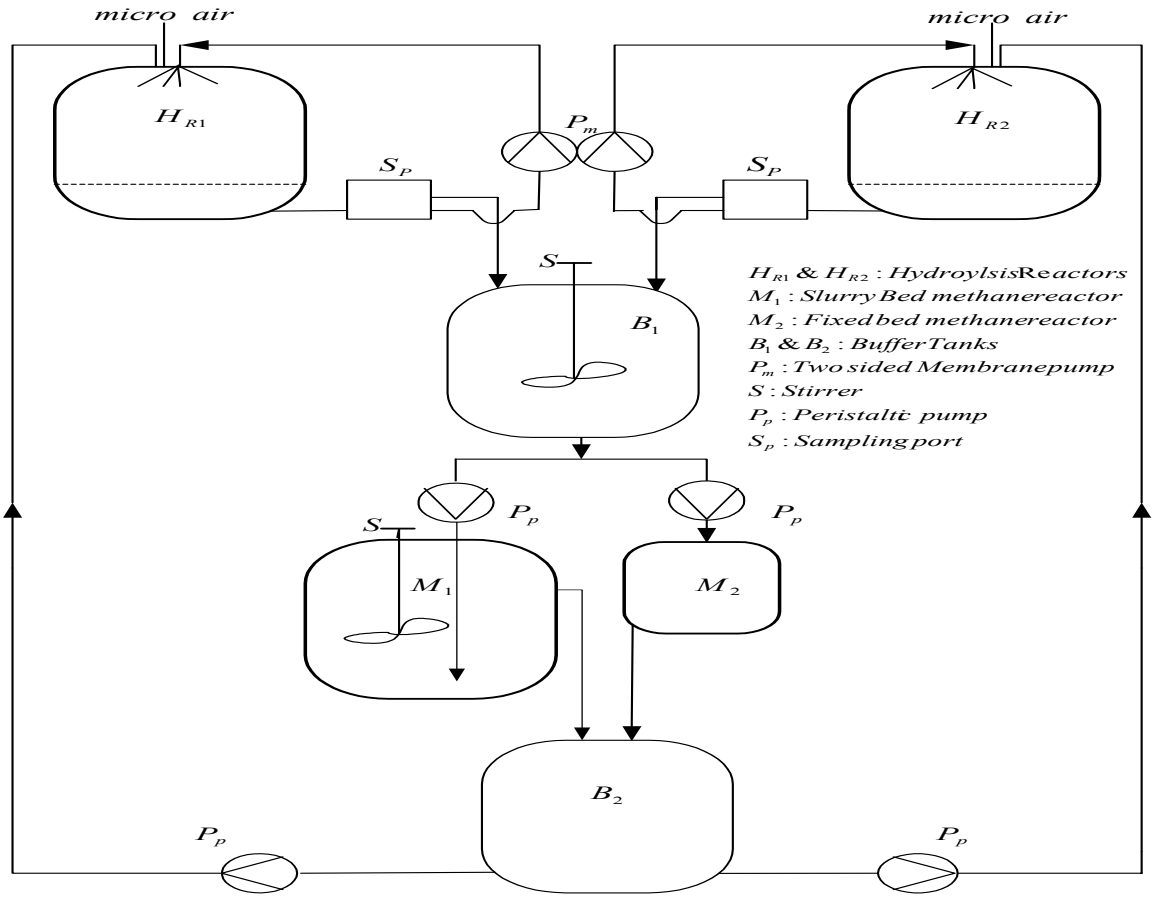


Figure 5.2. Schematic representation of the reactor set-up.

The cover of the reactor is provided with many access points for temperature and gas measurement, process water, and micro air entry. The waste bed rest on plastic sieve made of polyvinyl chloride (PVC) having the same diameter as the reactor with holes size of 5 mm in

diameter punched arbitrarily and placed 30 cm above the bottom of the reactor. A parallel set-up system (H_{R1} and H_{R2}) was employed which allows a repeated experiment to be run concurrently exploring sources of variability.

Fresh waste was slowly wetted using fresh tap water or effluent (treated water) after methanogenic process (liquid that has been exhausted of its COD content) from buffer B_2 with the aid of a pump (P_p) based on the predetermined flow rate required for that experiment. This was done continuously (12 periods per day) at a two-hour interval with pumping times (5-8mins). The aim was not to deliver the dilution water too quickly as this will cause excessive channelling and reduce the effective contact time between the leachate and the waste bed. On the contrary, delivering the dilution water too slowly will also increase the contact time between acidic pockets and bacteria which may not be a favourable condition for the hydrolytic bacteria. Where higher flow rates were required, fresh water from the laboratory was added to set the amount of leachate required, or part replaced when the salinity goes high.

All subsequent experiments were started by using the leachate from previous experiment. Leachate from stabilized waste contains varied consortium of microorganisms that help hasten a balanced microbial community to be established in the fresh waste, which facilitate faster conversion of organic carbon.

Leachate withdrawal/recycling port (S_P) of about 15 litres by volume is attached directly to the reactor at the 10 l level for control and liquid sampling. It also ensures steady supply of liquid for recirculation. Leachate flow freely into this port while, supernatant overflow by gravity into an effluent tank placed beneath it. The remaining liquid in the port is semi-continuously pumped back into the reactor top using two 0.5 inch air-operated double diaphragm pumps (P_m) with metal casing, and thermoplastic diaphragms regulated at every 15 minutes (at 166 ml of leachate/sec) for a duration of 3 minutes. The continuously recycling of process effluent promotes adequate mixing and soluble solids removal from the waste bed. Every 15 minutes was assumed to be a reasonable time period for carrying out the pumping of leachate back to the reactor to further washed out soluble substrate generated within the waste bed.

The temperature of the hydrolytic reactors were maintained at 30 ± 2^{o}C and controlled by a thermostat boiler (240 W, TEG 005-02P series type, manufactured by Öko Plus-Germany), and sustained by heated copper coils around the reactor. The reactors were insulated to maintain the heat within the reactors.

The reactor temperatures were measured with PT 100 thermometers, measuring temperatures at vertical positions of the system and registered by a computer.

A HP VEE 4.0 – Lysi 07 software (written by chair of waste management) operating in MS windows was used for on-line monitoring of digesters. The on-line parameters monitored include; temperature of the hydrolysis and methane reactors, and the biogas flow rate of the methane reactors.

The methanogenic phase. The composition of the methanogenic phase include; a buffer tank (B_1), slurry (M_{R1}) and a fixed bed reactor (M_{R2}), treated liquid tank (B_2) and required liquid pumps (P_p) as shown according to the scheme in figure 5.2.2. All these reactors are polyethylene barrels similar to the one used for the hydrolysis reactors. Only the slurry bed and fixed bed methane reactors are insulated with styrene sheet and binded by cello tape.

The *buffer tank* (B_1) is a storage tank filled with the mixed effluent of the two hydrolytic reactors (H_{R1} and H_{R2}). It has a 120 L volume capacity with transparent level gauge and a peristaltic pump. Mixing was accomplished by a top mounted, directly coupled DC motor with two impeller vertical shaft extending approximately 40 - 60 cm distance from the bottom of the digester stirring at 45 rotations per minute. The liquid in the buffer tank was kept at a temperature below 13 ^{o}C.

The *slurry bed* methane reactor has a 120 L volume capacity, started with an inoculum taken from an anaerobically digested sewage sludge (4 % TS) at the waste water treatment plant in Cottbus which conforms to the start-up approach of (Stenstrom,1983). Mixing was accomplished similar to that of the buffer tank.

The *fixed bed* reactor was 60 l by volume capacity but reduced to volume of 20 l by plastic chip material packed within the reactor as support medium. This was used as a ***supplementary*** reactor to help treat large volumes of leachate coming from the two hydrolysis reactors. NB.The discussion of the results from the fixed reactor would not be emphasised.

The feeding of the methane reactors were delivered from the buffer tank to the methane reactor at every 4 hours through an adjustable Heidolph peristaltic pump (PD 5206). The (PD 5206) was later on replaced by a multi-channel Heidolph peristaltic pump (PD 5201). The inlet and outlet to the slurry and fixed bed methane reactors are at opposite ends and feeding was carried out semi-continuously, with the feed introduced at the bottom in the case of the slurry bed displacing an equal amount of effluent at the top and, in opposite directions in the case of the fixed bed reactor. The pumping time used was deemed appropriate based on predetermined slurry settling time of the slurry bed methane reactor to ensure minimum slurry wash out.

The temperatures of the methane reactors were maintained at 38±2^{o}C and controlled by a thermostat boiler (240 W, TEG 005-02P series type, manufactured by Öko Plus), and sustained

by heated copper coils around the reactor. The reactors were insulated to help maintain the heat within the reactors.

The covers of the reactors were provided with access points for gas measurement, liquid entry, and temperature device. Similarly the temperature and biogas production trend were recorded by a computer using HP VEE 4.0 – Lysi 07 software (written by the chair of waste management) operating in MS windows for on-line monitoring of the digesters.

5.4 Sampling campaign

5.4.1 Brief description of sampling campaign

Leachate pH, temperature, salinity and conductivity, the gas volume and composition were monitored daily. Leachate was sampled daily at a particular time of each day to ensure a homogenous, representative sampling. Samples were immediately stored in a refrigerator at -10 ^{o}C. There were exceptions where samples were taken ±4 hours of the daily sampling time. Solid samples were taken before and after digestion. A brief summary of the sampling campaign are given table 5.3. The parameter, the number of samples analysed per parameter per test period are also presented.

Table 5.3. Summary of sampling campaign for ten days test period

Parameter	No. of samples	Type of samples	Sampled Reactor
Liquid Phase			
pH	60	Grab	H_{R1},H_{R2},M_{R1},$M_{R2,}$ B_1,B_2
Temperature	40	Grab	H_{R1},$H_{R2,}$$M_{R1}$,$M_{R2}$
Conductivity/Sal	60	Grab	H_{R1},$H_{R2,}$$M_{R1}$,$M_{R2}$,$B_1$,$B_2$
Organic Acid	20	Integrated*	H_{R1},H_{R2},B_1,B_2
COD	20	Integrated*	H_{R1},H_{R2},B_1,B_2
BOD_5	2	Integrated**	B_1,B_2
TS	30	Integrated*	H_{R1},$H_{R2,}$$M_{R1}$,$M_{R2}$,$B_1$,$B_2$
IL	30	Integrated*	H_{R1},$H_{R2,}$$M_{R1}$,$M_{R2}$,$B_1$,$B_2$
NH_3	15	Integrated*	,M_{R1},M_{R2},B_2
Solid Phase			
TS	3	Grab	H_{R1},H_{R2}
IL	3	Grab	H_{R1},H_{R2}
TOC	3	Grab	H_{R1},H_{R2}
TKN	3	Grab	H_{R1},H_{R2}
Gas Phase			
Biogas flow rate	Daily reading	Direct meter readings	M_{R1},M_{R2}
Biogas composition	Daily reading	Direct meter readings	M_{R1},M_{R2}, H_{R1},H_{R2}

*Samples of preceding and the previous day were integrated into a single volume. **Samples of each day were added to each other in a cumulative manner to form a single volume probe.

5.4.2 Solid phase sampling

Input and Output waste sampling. The solid samples were obtained only at the beginning and at the end of each experiment. In all the experiment, the same sampling protocol was used for both the waste that was loaded into the reactors and the degraded waste unloaded from the reactors. Since more than one reactor was normally loaded at a time, a common sample was taken. At the time of unloading, the waste from each reactor was sampled separately. The remaining digestate after sampling was discarded in a campus bin. A grab sample of 1.5-2.0 kg (wet mass) of thoroughly mixed input waste was taken for characterization. The samples were placed in silver pan containers and taken to the analytical laboratory for analysis.

5.4.3 Liquid sampling

Liquid samples were taken daily before noon from the following reactors; the two hydrolysis reactors (H_{R1} and H_{R2}), the two methane reactors (M_{R1} and M_{R2}), and the two buffer tanks (B_1 and B_2). An amount of 120 ml grab from each sampling unit was taken into 250 ml sample containers. Each sampling unit was thoroughly stirred before sampling. Two days (day before and the day after) samples were integrated into a single volume probe for parameter analysis of chemical oxygen demand (COD), organic acid (OA), total solid (TS), and loss on ignition (LOI). Samples for biological oxygen demand (BOD) were obtained from the two buffer tanks B_1 and B_2. Each analysis samples for B_1 and B_2 were obtained by adding daily samples together in a cumulative manner as one large single probe. A number of direct physical and chemical parameters were measured as part of process monitoring approach.

Direct and instant physical and chemical parameter measurement. These were measurements carried out with the aim of gaining quick information about the status of the anaerobic digestion process.

The physical and chemical parameters measured as a process monitoring strategy include; pH, temperature, conductivity and salinity were conducted daily on samples before processing (integration). No gas phase samples were made but rather direct biogas flow rate was measured daily through a gas meter installed upstream and its composition also analysed directly using an appropriate equipment. A short description of the procedure is given below.

pH and temperature measurements were made on grab samples taken from the two hydrolysis reactors (H_{R1} and H_{R2}), the two methane reactors (M_{R1} and M_{R2}), and the two buffer tanks (B_1 and B_2). The measurement were carried out by inserting the electrode of a portable pH meter (WTW 315i) into the sample liquid which displays the pH and temperature values instantly.

Conductivity and salinity measurements were made on grab samples taken from the two hydrolysis reactors (H_{R1} and H_{R2}), the two methane reactors (M_{R1} and M_{R2}), and the two buffer tanks (B_1 and B_2). The measurement was carried out by inserting the electrode of a portable conductivity/salinity meter (WTW LF 340) into the sample liquid which displays the conductivity and salinity values instantly.

Biogas flow rate and composition were measured direct through a gas meter (Ritter TG 05/5 Mechanical clock) installed upstream of the two methane reactors (M_{R1} and M_{R2}), while its composition (CH_4, CO_2 and O_2) was analysed directly using portable Ansyco GA-94^{TM} landfill gas analyser respectively. The basic principle behind the CH_4, CO_2 measurement is simple spectroscopy (near infra red) whiles O_2 is measured electrochemically.

Online monitoring. Daily temperature and biogas flow rate fluctuations were monitored through a software operated in Microsoft windows. This approach provided a meaningful and easily-interpreted signal about the stability of the fermentation process on a day to day basis.

5.5. Various analytical laboratory analyses

A summarized description of the various analyses and method employed in the study is shown in table 5.4.

Table 5.4. Summary of analytical techniques and laboratory equipment used

Parameter	Method	Equipment
PH	DIN 38404-C5*	WTW 315i PH meter
Temperature	DIN 38404-C4*	WTW 315i PH meter
Conductivity/Sal	DIN EN 27888*	WTW LF 340
OA	Distillation	Gerherdt vapodest distillator, Hot plate, titration equipment
COD	Cell Test (standard method 5220D* and ISO 15705*)	Reaction cells, Merck Thermoreactor TR 420, WST Photolab spectrometer, Mini Spin Centrifuge
BOD_5	Dilution method (DIN EN 1899-1,*ISO 5815 and Standard method 5210B*)	Winkler bottles, WTW Oxi 538 amperometric sensor, incubator, Saskia Hochvacuum aeration equipment
TS	DIN 38409-3*	Ceramic crucible, Analytical balance, Drying oven
IL	DIN 38409-3*	Ceramic crucible, Analytical balance,Furnace
TOC	DIN 38409-3*	Crucible, High temp oven, Furnace, Analytical balance
TKN	Kjeldahl DIN 38409-27*	Kjeldahl digestor, Distillator, Titration device
NH_3		
Biogas	Mechanical (wet gas meter)	Ritter TG 05, GmbH Mechanical clock
Biogas composition	Spectroscopic	Portable Ansyco GA-94^{TM} Land fill gas analyser

* standard code

A detailed description of the individual parameters and procedures are also provided below.

Solid phase samples. The solid samples were obtained only at the beginning and at the end of each experiment as described earlier on. A sample of 1.5-2.0 kg (wet mass) was weighed on a gram analytical balance and taken for characterization.

- ***Total solid (TS):*** The total solid is the raw estimation of all organic and inorganic matter content in the original sample. This parameter measures the substrate concentration in the feed obtained as residue upon water evaporation at a temperature of 105^{o}C. Total solids analysis was measured by drying the wet waste (1.5 -2.0 kg) in a drying oven at 105^{o}C for 16 - 32 hours. The sample was taken out of the oven and placed in a hood to cool to room temperature. Percentage dry matter measured as the remaining weight of sample, after drying, and is expressed as percentage of the wet sample according to equation (5.11).

$$\%TS\left(dry\ matter\right)=\frac{\left(M_{ws}-M_{ds}\right)}{\left(M_{ws}-M_{tara}\right)}*100 \qquad 5.11$$

  Where M_{ds} is the mass of the dried sample with container; M_{tara} is the mass of the empty metal container; M_{ws} mass of the wet sample with container.

Before any further analyses were carried out, the dried solid waste was finely ground to an average particle size of 0.5 mm. The entire samples were thoroughly mixed and homogenized using spatula before sub sampling.

- ***Loss on Ignition (LOI)***: Loss on ignition is an approximation of the organic fraction in the dry matter. It is a parameter that characterizes the fraction of the solid matter which can be driven off as gas at a temperature of 550^{o}C. Loss on ignition was determined by ashing the dried and grounded sample in a furnace at 550^{o}C for 2 hrs. An approximate amount of 50±1 g of the dried ground sample was placed in a ceramic crucible and allowed to burn in the furnace. Samples were removed from the furnace and allowed to cool in a desiccator with an active desiccant to room temperature. The loss on ignition was calculated according to equation (5.12).

$$\%IL\left(TS\right)=\frac{\left(M_{ds}-M_{as}\right)}{\left(M_{ds}-M_{tara}\right)}*100 \qquad 5.12$$

  Where M_{ds} is the mass of the dried sample with crucible; M_{as} is the mass of the ashed sample; M_{tara} mass of the empty crucible.

- ***Total Carbon (TC):*** This parameter summarizes all carbon compounds in a sample independent of their biological availability. This parameter was determined by oxidizing all the carbon in the organic compound to carbon dioxide and spectroscopically measuring the carbon dioxide by infra red as an equivalent of total carbon present in the

sample. This was achieved by thermally combusting the samples at high temperatures of 1000^{o}C in an ELTRA type of oven in the presence of oxygen at a required pressure. ***Procedure:*** In order to measure the total organic carbon present, the amount of both total carbon and inorganic carbon present in the solid sample were required. Dried milled (0.5 mm size) sample is placed in a porcelain boat (60-120mg) and combusted in the high temperature oven and subsequently measure the evolved carbon dioxide by a spectrometer (Micro N/C type). Each measurement was repeated thrice and the average value taken as gram total carbon/kilogram sample. Similarly, the same procedure was followed; using the ashed sample obtained after loss on ignition for determination of inorganic carbon. The total organic carbon (TOC) was calculated from the results of Total Carbon (TC) and Total Inorganic Carbon (TIC) obtained. And this was done according to equation 5.13.

$$TOC\ (g/kg) = (TC - TIC) \qquad 5.13$$

- ***Total Kjeldahl Nitrogen (TKN):*** This is an analysis to determine both organic nitrogen and the ammonia nitrogen present in the solid sample. The Kjeldahl digestion converts nitrogen compounds (proteins, amines and organic compounds) into ammonia compounds. Free ammonia is released by addition of caustic, which is then expulsed by distillation and subsequently titrated. ***Procedure:*** The Kjeldahl method was followed. Approximately, 250 mg of a ground sample; 15 ml of concentrated (98%) sulphuric acid and a Kjeldahl tablet (salt and catalyst) was digested at 360 ^{o}C for an hour. Digestion burners are turned off and the digested sample is allowed to cool down to temperatures below 250 ^{o}C. The digested sample was diluted with 20 ml of distilled water. This was further treated with concentrated (2M) sodium hydroxide to release free ammonia, which is expulsed by distillation into 20 ml of 0.1M Boric acid with 0.5 ml of mixed indicator and subsequently titrated with 0.1M hydrochloric acid. A duplicated determinations were always carried and the average value taken.

Total Organic Nitrogen as a percentage value was obtained from equation (5.14):

$$TON\left(\%\, m/m\right) = (V_a - V_b) * K_n * \frac{100}{M_s} \qquad 5.14$$

Where V_a is the titre value of the HCl; V_b is the titre value for a blank sample (0.23 ml); K_n a constant value of 1.4, for the conversion of a millilitre of HCl to millilitre Nitrogen already measured in the laboratory; M_s mass of sample.

Liquid samples. Analysis was carried out on the liquid samples to determine the amount of hydrolytic and fermentation products leached out into solution in the first stage of the anaerobic digestion

Liquid samples in the form of process water were sampled (120 ml) daily from H_{R1}, H_{R2}, B_1, B_2 and M_{R1} and M_{R2} into plastic sample bottles. Samples of the day before and after were combined as a single sample. Before analysis, the samples were immediately kept in a refrigerator at a temperature of -10 degrees Celsius to maintain the chemical and physical properties that it possessed at the time of collection. Sample holding times were 3-7 days. Liquid samples for BOD_5 analysis were taken from the two buffer tanks B_1 and B_2. Daily samples were added to each in a cumulative manner. The following analysis was carried out on the liquid samples.

- ***Total solids:*** As stated earlier on, samples of the first and the second day were combined together as single sample for daily liquid sampling from reactor H_{R1}, H_{R2}, M_{R1}, M_{R2}, B_1, B_2. Similarly, the same sample preparation was applied to the rest of the days for the entire test period. i.e. the third and the fourth, fifth and the sixth, etc to the tenth day. ***Procedure:*** The procedure followed for liquid sample measurement is the same except that, approximate amount of 50-60 g of liquid sample was placed in a ceramic crucible and dried at 105 ^{o}C overnight (at least 16 hrs) in a drying oven. The dried sample was cooled to room temperature in a desiccator. The total solid was calculated from equation (5.15).

$$\%TS = \frac{(M_{ls} - M_{ds})}{(M_{ls} - M_{tara})} * 100 \qquad 5.15$$

  Where M_{ds} is the mass of the dried sample with crucible; M_{tara} is the mass of the empty crucible; M_{ls} mass of the liquid sample with crucible.

- ***Loss on Ignition:*** The loss on ignition was determined by ashing the dried sample at 550^{o}C in a furnace for 2 hours using the same sample after total solid determination. The calculation was done according to equation 5.16.

$$\%IL(TS) = \frac{(M_{ds} - M_{as})}{(M_{ds} - M_{tara})} * 100 \qquad 5.16$$

  Where M_{ds} is the mass of the dried sample with crucible; M_{as} is the mass of the ashed sample; M_{tara} mass of the empty crucible.

- ***Chemical Oxygen Demand (COD):*** This is a measure of all the organic matter in the substrate found in the liquid. The cell test method was followed. COD laden water sample is oxidized with hot sulphuric solution of potassium dichromate, with silver sulphate as a

catalyst. The concentration of the resulting green solution (Cr^{3+} ions) was determined photometrically. ***Procedure:*** The COD measurement was made on samples from H_{R1}, H_{R2}, B_1 and B_2 according to the sampling technique of integrating two days samples as a single probe. A dilution of 1:10 was prepared before determination. For low laden COD samples, no dilution was done. 1 ml of the pre-treated sample was taken and placed in a reaction cell. The content of the cell was vigorously mixed and then placed in a preheated thermoreactor (Merck Thermoreactor TR 420) for 120 min at 148^{o}C. The cells are removed and shaken after ten minutes and allowed to cool to room temperature. Measurement was carried out photometrically in a WST Photolab spectrometer as mg/l COD. Samples from buffer B_2 were centrifuged at 13400 rpm for 7 min to removed sludge influence on undegraded COD.

- ***Organic Acid (OA):*** organic acid is the main fermentation products of the first stage measured cumulatively as acetic acid. Total soluble organic acid, measured as acetic acid was determined by distillation method. Basically, the liquid probe is treated with concentrated acid and distilled. The organic/inorganic acids present in the sample are vaporized and subsequently condensed. The condensed solution was further boiled on a hot plate to drive off unwanted acids (inorganic acids) in the form CO_2, the resulting solution was cooled and titrated with a base solution. Determination was carried out on samples from reactor H_{R1}, H_{R2}, B_1 and B_2 (similar to samples used for the COD measurement). ***Procedure***: 5 ml of concentrated orthophosphoric acid (98%) was added to an approximate amount of 100±1 ml of sample and distilled for 16.65 minutes. The condensed liquid was boiled on a hot plate for 10 minutes to remove as much inorganic substances in a form of gases; for example CO_2 etc. The resulting solution was allowed to cool to room temperature under a hood. Five drops of phenolphthalein indicator was added to the cooled liquid and titrated with 0.1 M sodium hydroxide. Organic acid as acetic acid was calculated according to (5.17) below.

$$OA\left(g/l\right)=\left(\frac{V_{NaOH}*M_{NaOH}*MM_{CH_3COOH}}{V_{Liquid\ sample}}\right) \qquad 5.17$$

Where V_{NaOH} is the titre value; M_{NaOH} is the molar concentration of sodium hydroxide; $MM_{CH3COOH}$ is the molar mass of the acetic acid; $V_{liquid\ sample}$ is the volume of the sample.

- ***Biological Oxygen Demand (BOD)***: It is the concentration of biodegradable organic matter present in a sample of liquid. The method used measures the consumption of oxygen related to the biological activity. The BOD is represented as the difference in the

oxygen concentration at the beginning of the incubation and after the 5-day incubation under consideration of the respective dilution ratios as well as of the blank value of the dilution water. ***Procedure:*** The dilution method was followed. Dilution water was prepared by adding 10 ml each solution of already prepared phosphate buffer solution (pH 7.2), magnesium sulphate heptahydrate solution (22.5g/l), calcium chloride solution (27.5 g/l) and ferric (III) chloride hexahydrate solution (0.25g/l) to 5000 ml distilled water and further diluting with additional 5000 ml. Inoculation was not required since initial trial with inoculation indicate too much bacteria and producing negative results. The resulting solution was aerated for an hour with suitable equipment (Saskia Hochvacuum). A ***Standard solution*** was prepared by weighing 15.0 mg each of dried (105^oC for 1 hr) and cooled L-Glutamic and D-Glucose into a 100 ml volumetric flask and diluting to the mark with distilled water. ***Control sample:*** 20 ml of the glucose-glutamic acid standard solution was pipetted into 1000 ml plastic volumetric flask and diluted to the mark the aerated solution. ***Blank sample*** was prepared by filling 1000 ml of the aerated solution into 1000 ml volumetric flask without any probe. ***Analysis sample*:** Duplicate serial dilutions (1:1000; 1:10000; 1:100000) of high COD laden probe from buffer B_1 were prepared in a 1000 ml volumetric flask and made to the mark with aerated solution. Similarly, duplicate serial dilutions (1:500; 1:1000) of low laden COD of treated water from buffer B_2 were also prepared. To each of the serially diluted solutions, control and the blank solutions, 5 mg of nitrification inhibitor (allylthiourea) were added and shaken. Measurement samples were prepared by filling Winkler bottles with the serially diluted solutions. Oxygen concentration in each Winkler bottle was measured using oxygen sensor. The sample bottles were subsequently incubated for 5 days ± 2h at 20 ^oC in the dark. After incubation, the oxygen concentrations in the bottles were determined again. The BOD for each sample is calculated according to the following equation:

$$BOD_5 = \left[(C_1 - C_2) - \frac{V_t - V_e}{V_t} * (C_3 - C_4) \right] * \frac{V_t}{V_e} \qquad 5.18$$

Where:

C_1 is the concentration of dissolved oxygen (mg/l) in an analysis solution at zero time

C_2 is the concentration of dissolved oxygen (mg/l) in the same analysis solution after 5 days

C_3 is the concentration of dissolved oxygen (mg/l) in the blank test solution at zero time.

C_4 is the concentration of dissolved oxygen (mg/l) in the blank test solution after 5 days.

V_e is the volume of sample (mg/l) that was used for the production of the analysis solution in question

V_t is the total volume (ml) of this analysis solution.

Statistical analysis of process data were analyzed by descriptive statistics (i.e. variation ranges, arithmetic averages, standard deviations, and coefficient of variation). Correlations between variables were performed and behavior of different parameters with time was plotted. The Excel 2003 (Microsoft Corporation package) and Sigma plot 10.0 software were used to carry out all statistical analyses of data and figures.

5.6 Individual experiments carried out

As already described in table 5.1 above, individual experiments were carried out with particular attention paid in reproducing the working conditions already tested. As regards to statistical validity and reliability of results, each test was repeated by carrying out the same test in parallel. The two microaerophilic reactors (H_{R1} and H_{R2}) were filled generally with 20 kg of simulated waste corresponding to 12-25 % total solid. Dilution water of 20-35 l/d (1-1.75 l/kg input material .d) of treated liquid or fresh water was used. Digestion was carried out up to 10 days except experiments 6.6.3 and 5.6.6 where longer duration was desired.

5.6.1 Start-up methodology

The study included a start-up phase, in which the micro aerobic digester was started with no inoculum except the case of the slurry bed methane reactor where a seed from anaerobically digested sewage sludge was used. The fixed bed used later was already in use.

Inoculation phase: Seeding material was obtained from an anaerobically digested sewage sludge (4 % TS) from a waste water treatment plant in Cottbus, Germany. A total sludge volume of 55 l (equivalent to 50% of the reactor effective volume) was placed into the 120 l barrel methane reactor and top up to the 110 l mark (working volume) with tap water.

Start-up. Initially, the slurry bed was fed with COD laden (about 5000 mg/L) hydrolysed liquid from an on-going experiment in the laboratory at an initial flow rate of 10 litres per day corresponding to HRT of 11 days until the gas production rate and composition stabilizes. (Approximately 5 days). After this, the seeded sludge was exposed to further selection process by the application of increasing flow rates such as 16, 20, 24 litres leachate per day of COD laden (about 5000 mg/L) hydrolysed liquid until a new level of gas production rate and composition (average CH_4 content of 70%) were obtained approximately 2 weeks indicating that the methane

reactor had been active in methanogenesis. Following this initial acclimation period, experiments with UMSW began. The result of this process was not included in the write up. The procedure was aimed at adapting the microorganisms to the substrate and also improving settling properties of the remaining biosolids particles.

5.6.2 Effect of volumentric flow rate on particulate matter degradation

Solubilization of particulate matter occurs in the liquid phase, therefore, wetting the waste with an **appropriate** amount of water was very essential to hasten this process and also allow the bacteria to move freely within the reactor.

Experimental design - a dilution design was developed which required that the hydrolytic reactors be operated at the water flow rate of 1, 1.13, 1.25, 1.38, 1.5 and 1.75 l/kg input waste.day, corresponding to HRTs of 0.61, 0.54, 0.49, 0.44, 0.41, and 0.35 day respectively. The digesters were first operated at the lowest water dilution and greatest retention time and as the experimental phase continued the dilutions were increased. Table 5.5 shows the characteristics of each experiment. The dilutions were adjusted volumetrically, by controlling the flow rate of the influent process water into both hydrolysis and methane reactors.

Table 5.5. Average flow rates and ralated HRT values applied during the test.

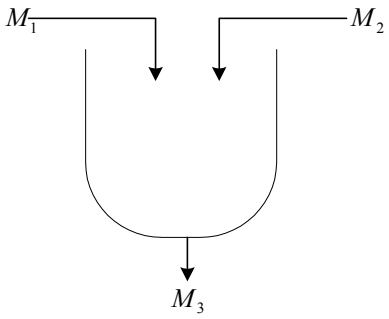
Experiment	Av. flow rates in H_{R1}/H_{R2} (l/d*kg)*	Av. HRT in H_{R1}/H_{R2} (d)	Av. HRT in M_{R1}/M_{R2} (d)	Temp in H_R/M_R (o^c)	Waste UMSW/Mkt**	No of run
Expt 5.6.1.1	1.00	0.61	5/3	30/36	UMSW/TLO	2
Expt 5.6.1.2	1.13	0.54	4.44/2.67	31/38	UMSW/CTO	2
Expt 5.6.1.3	1.25	0.49	4/2.4	30/37	UMSW/COA	2
Expt 5.6.1.4	1.38	0.44	3.64/2.1	30/37	UMSW/TSO	2
Expt 5.6.1.5	1.50	0.41	3.33/2.0	30/38	UMSW/OTL	2
Expt 5.6.1.6	1.75	0.35	2.86/1.71	30/37	UMSW/TOL	2
Expt 5.6.1.7*	Varied↓	Varied↓	Varied↓	32/38	UMSW/OTL	2

* Average flow rate of process water in liters water/kg input material/day ** The pumping liquid flow rate was changed in a stepwise manner (±12.5%) in every two days during the test period (↓stepwise decrease). **Fruits and vegetables of the market waste fraction in a decreasing order of abundance. A=Apple, C=Cabbage, L=Leaves, O=Oranges, P=Potato, T= Tomato.

The low flow rate applied at the beginning especially in the case of the methane reactor was aimed at adapting gradually the seeded biomass to design loading rates and also at preventing wash out of biosolids from the reactor. The flow rate was gradually increased based on steady state behaviour of the process monitoring parameters for a given operating conditions.

The *goal* of the whole procedure was to establish the optimal dilution liquid required for an optimum solublization and leaching in the hydrolytic reactor and the subsequent biogas production by the methane reactor at various influent organic strength at the applied operating conditions.

The dilution water required for the hydrolytic process was obtained based on the following mass balance approach;



Where;
$M_1 = biowaste$
$M_2 = water$
$M_3 = final\ mixture$

Let;
$X_1 = water\ content$
$X_2 = 100\%$
$X_3 = water\ content$

Total mass balance

$$M_1 + M_2 = M_3 \qquad 5.19$$

Component balance

$$M_1 * X_1 + M_2 * X_2 = M_3 * X_3 \qquad 5.20$$

From equ (2);

Finally;

$$M_2 = M_1 \frac{(X_3 - X_1)}{(1 - X_3)} \qquad 5.21$$

For example;

Let;
$M_1 = 20\ kg$
$X_1 = 0{,}75$
$X_2 = 1$
$X_3 = 0{,}9$

$$M_2 - M_2 * X_3 = M_1(X_3 - X_1)$$
$$M_2(1 - X_3) = M_1(X_3 - X_1)$$

$$M_2 = 20 * \frac{(0{,}9 - 0{,}75)}{(1 - 0{,}9)} = 20 * 1{,}5$$

$M_2 = 30\ kg = Amount\ of\ dilution\ water\ required$

Process performance: The reactor behaviour was monitored during the fermentation period through different parameters. Temperature, pH, OA, COD, BOD_5, TS, IL, NH_3, conductivity and salinity were monitored in the liquid phase for both the hydrolysis and the methane stages. TOC, IL, TS and TKN were performed on the solid samples before hydrolysis. Biogas flow rate

readings were taken from gas meter installed upstream of the reactor and instant biogas composition measure. Only biogas composition was monitored for the hydrolysis stage since biogas production can be negligible. Section 5.4 summarizes the sampling programmes and section 5.5 describes in detail the various analytical techniques for parameter analysis. The same process performance criteria were applied to all the subsequent experiments.

5.6.3 Solid retention time and degradation rate

Solid retention time with respect to the test is defined as the average time that the input solid material remains inside the hydrolytic reactor. This concept includes the particulates that enter the digester as well as those that are generated inside and in addition to the inert materials.

Digestions of the simulated waste of 50 part-by-weight UMSW and 50 part-by-weight market waste were performed at 7,10 and 14 days solid retention times (SRTs). In table 5.6 are the characteristics of the experiments. The main aim was to determine the most appropriate SRT for the digestion of the simulated waste in the first stage of a mesophilic digestion process.

Table 5.6. Process parameters applied during the experiment

SRT in HR (d)	Flow rate (l/kg*d) H_{R1}/H_{R2}	Av HRT (d) H_{R1}/H_{R2}	Av HRT (d) M_{R1}/M_{R2}	Temp(^{o}C) H_R/M_R	Waste UMSW/Mkt **	No. of runs
7	1,25	0.49	4/2,4	30/38±2	UMSW/L	2
10	1,25	0.49	4/2,4	30/38±2	UMSW/COA	2
14	1,25	0.49	4/2,4	30/38±2	UMSW/L	2

**Fruits and vegetables of the market waste fraction in a decreasing order of abundance. A=Apple, C=Cabbage, L=Leaves, O=Oranges.

5.6.4 Temperature variation and the extent of degradation

Three temperatures (ambient, 30^{o}C and at 35^{o}C) were tested with the objective of determining whether the degradation observed at ambient temperature and at 35^{o}C have significant effect on particulate matter degradation at the hydrolytic stage. The test is based on the hypothesis that the activity of the microorganisms does not change much at ambient temperature, while the activity of the microorganisms is increased appreciably at 30 ^{o}C and 35^{o}C.

The test and its operational conditions are described hereunder.

Table 5.7. Characteristics of the experiment

Temp(^{o}C) H_R/M_R	Flow rate (l/kg d) H_{R1}/H_{R2}	Av. HRT (d) H_{R1}/H_{R2}	Av. HRT (d) M_{R1}/M_{R2}	Waste: UMSW/Mkt **	No. of runs
Ambient temp: 26/38±2	1,25	0.49	4/2,4	UMSW/LT	2
30/38±2	1,25	0.49	4/2,4	UMSW/COA	2
35±1/38±2	1,25	0.49	4/2,4	UMSW/BL	2

*Fruits and vegetables of the market waste fraction in a decreasing order of abundance. A=Apple, B=Berry, C=Cabbage, L=Leaves, O=Oranges, T= Tomato.

5.6.5 Effect of pre-processed feedstock on digestion

It is has been hypothesized that separately collected waste streams often can be treated more efficiently both in technical and economic respects, and with a higher degree of environmental sustainability as they are more concentrated and have a more homogenous composition (Mata-Alverez, 2003). Therefore, in this investigation the input material for the various tests were pre-treated to enhance the extent of bioconversion in the first stage, produce more biogas in the second stage and, at the same, reduce the digestion time of the entire process (Veeken et al., 1999). Different substrates/input materials were obtained through manual and mechanical pre-treatment processes, and were tested. Among the most important separation and pre-treatment processes, size reduction, manual sorting and dry mechanical separation were employed. The waste material was mechanically reduced in size with the aid of a shredder. The dry mechanical separation was carried out with the aim of separating a mixture of different materials into two or more size fractions using vibrating conveyor belt screen system with different kinds of sieves with apertures of different width.

In terms of cost, mechanical treatment appears to be the most economic method compared with other pretreatment methods. The various pre-treated input material used in this experiments is as shown in Table 5.8.

Table 5.8. Summary of test characteristics and their process conditions.

Type of pretreatment	Flow rate (l/d*kg)	Temp (^oC) $H_{R1\&2}/M_{R1\&2}$	Av. HRT (d) H_{R1}/H_{R2}	Av. HRT (d) M_{R1}/M_{R2}	Waste UMSW/Mkt *	No. of runs
Simulated	1,25	30/38±2	0.49	4/2,4	UMSW/CLC	2
Ideal waste	1,25	30/38±2	0.49	4/2,4	UMSW/ CLC	2
Market waste	1,25	30/38±2	0.49	4/2,4	UMSW/ATC	2
Shredded	1,25	30/38±2	0.49	4/2,4	UMSW/TOA	2
Mech sorted (8-40mm)	1,25	30/38±2	0.49	4/2,4	UMSW/APC	2
Mech sorted (40-120mm)	1,25	30/38±2	0.49	4/2,4	UMSW/LOA	2
Manually sorted (8-40mm)	1,25	30/38±2	0.49	4/2,4	UMSW/TCA	2

*Fruits and vegetables of the market waste fraction in a decreasing order of abundance. A=Apple, C=Cabbage, C`=Carrot, L=Leaves, O=Oranges, P=Potato, T= Tomato.

The goal of these experiments was to evaluate the influence of the various pre-processed substrates on the biodegradability of organic substrate, and ascertain whether a simple mechanical pretreatment of the UMSW was required to enhance biogas recovery.

Input material of 20 kg was used in each experiment respectively. And also the same process conditions were applied for all treatment methods.

Simulated waste. This type of waste was obtained in accordance with equations 5.7-5.10 shown above.

(a) Unsorted fraction

(b) Finally blended input material

Figure 5.3. Simulated waste characteristics

The 'Ideal waste' (Control). This experiment was a control test. This test was carried out using physically "clean" UMSW materials as shown in figure 5.4 with chopped market waste in a ratio of 65 parts-by-weight and 35 parts-by-weight UMSW excluding the putrescible fraction. The goal was to evaluate the process performance from any contamination.

The different parts of material used as input material is shown below.

(a) "Clean" unsorted UMSW

(b) Chopped market waste fraction

Figure 5.4. The characteristics of the ideal waste

Market waste (source sorted). The hydrolysis reactor was charged with 20 kg of fruit and vegetable waste chopped to 8-40 mm-size pieces as shown below in figure 5.5.

Nearly 100% of the feed was organic in nature as indicated by ignition loss of 91%.

Figure 5.5. Chopped fruit and vegetable waste

Shredded waste. This type of input material was obtained by shredding the original simulated waste. The digester feed consist of 50 part-by-weight of the UMSW and 50 parts-by-weight market waste. The raw 50 part-by-weight of the UMSW was coarsely (8-40mm) shredded to provide an increased surface area and also a high organic waste stream. Stones, metals, large pieces of wood and glass were hand removed before shredding.

Finally, the blending was done by adding a hand chopped market waste (8-40mm) to the shredded UMSW. A final blended digester material obtained is as shown in figure 5.6.

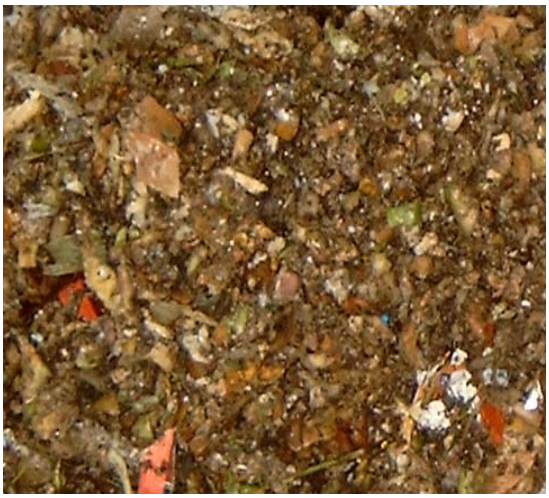
(a) Shredded waste

(b) market waste fractions before blending

Figure 5.6. Characteristic of the shredded waste

Manually sorted input material. A digestion was carried out using an input material prepared by manually sorting out undesirable materials such as plastic, stones, glass, metal and clothing.

A blend was finally prepared by 50 parts-by-weight market and 15 parts-by-weight sorted biowaste. Figure 5.7 shows the blend. The objective of this experiment was to evaluate the biogas production efficiency of the process in the absence of physically hindering materials.



(a) Manually sorted biowaste

(b) chopped market waste before blending

Figure 5.7. Characteristics of the source sorted waste.

Mechanically sorted fractions. Fractions (8-40 mm and 40-120 mm) from the mechanical separation were obtained from the process consisting of the following successive steps;

- Manually emptying of bagged refuse onto a conveyer belt.
- Sieving of the various fractions according to the principle of "fall-through".

Basically, the incoming commingled wastes are packed mostly in plastic bags. Therefore the bags are cut and emptied onto the conveyor belt where they are separated according to size.

A blend was finally prepared by 50 parts-by-weight market and 15 parts-by-weight of the sorted biowaste of size 8-40 mm. Similarly, a second blend was prepared which is made up of 50 parts-by-weight market and 50 parts-by-weight of the sorted biowaste of size 40-120 mm.

The various fractions of waste are shown in below in figure 5.8.

(a) 8-40 mm fraction

(b) 40-120 mm fraction

Figure 5.8 The two size fractions obtained from different sieve sizes

5.7 Single stage anaerobic digestion

This type of system is a one stage process having the entire processes, hydrolysis/acidogenesis and the acetogenesis/methanogenesis taking place simultaneously in one reactor.

The hydrolysis/acidogenesis and acetogenesis/methanogenesis processes take place within the waste bed and in the leachate. The hydrolysis is achieved by spraying the waste bed with biologically active liquid. The waste is acidified and the soluble components are leached out. The resulting leachate is recycled over and over the waste bed to promote further leaching and sufficient moisture for bacterial growth thereby increasing degradation.

5.7.1 Preliminary study with the single stage reactor

This experiment was carried out generally to test the fermentability of UMSW before tests with simulated waste started. The result of this preliminary study was published in the proceedings of "Waste 2004"conference held in the UK. A poster to this publication is included in the appendix (page 174). Table 5.9 shows the characteristics of the test conditions and brief summary of results is provided below.

Table 5.9. Characteristics and test carried out

Feedstock	Seed material	No. of runs	Temp	SRT
Fresh UMSW	Fresh inoculum	1	36±2	23
Fresh UMSW	leachate from previous test	1	36±2	23
Part of digestate from previous test+fresh UMSW	leachate from previous test	1	36±2	23

Summary of the results obtained shows that a total of 10 - 60 l biogas/kg TS with methane quality in the range of 30 – 69% was achieved 23 days after the start of three consecutive experiments carried out using UMSW as feedstock. On stabilization of digestion, daily amounts of 1.0 – 13.5 l biogas/l digester/day were produced respectively. In conclusion, the amount of biogas produced using the single stage digester was considered insufficient and the retention time was too long (23 days). Therefore, this limits the potential of the single stage digester for the treatment of UMSW.

5.8 Summary

In this chapter, four hypothesis were tested on the biomethanization of UMSW which includes, effect of water flow rate (dilution), solid retention time, temperature variation and various pre-processed substrate materials. Also included were detailed analytical procedures employed for sample analysis.

The next section describe the findings obtained from the laboratory-scale biomethanization of UMSW using the double-stage digestion approach. The analysis and evaluation are presented in a chronological order to describe the performance of the several strategies imposed in order to achieve the objectives of the study.

6 EVALUATION AND DISCUSSION OF RESULTS

6.1 Mass and component balances around the reactor set-up

This section presents the flow of materials within the entire reactor system, the hydrolysis reactor and the methane reactor.

6.1.1 Mass balance for the entire process

The material flow through the entire system is illustrated in the flow diagram in figure 6.1.

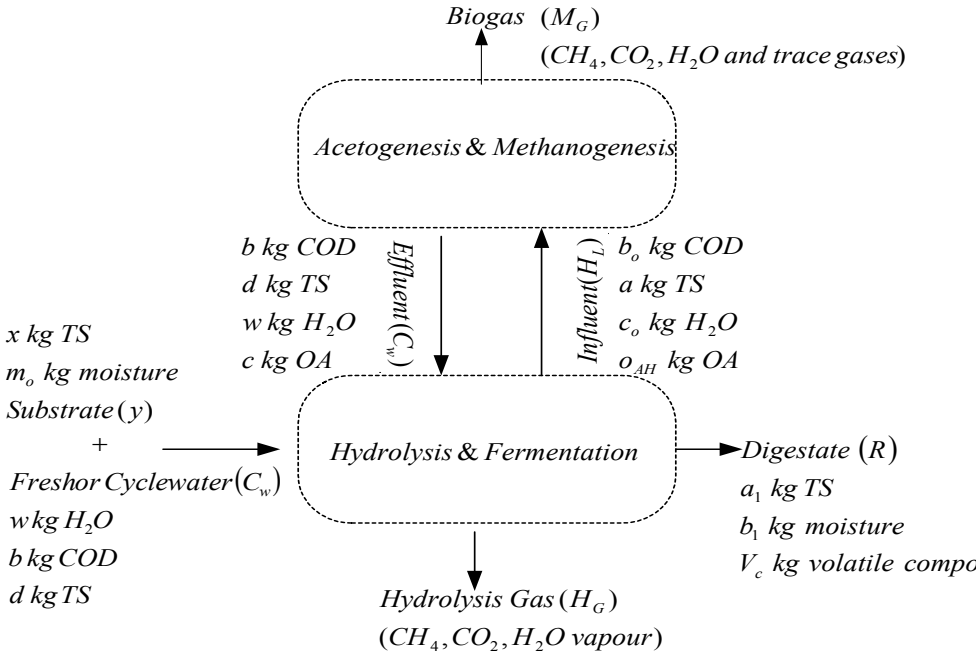


Figure 6.1. Material flow around the entire double-stage system.

Total mass balance

Let M represent mass.

Then,

$$[M_{substrate}] + [M_{freshWater}] = [M_{rest}] + [M_{Cyclewater}] + [M_{biogas}] + [M_{hydrolysisGas}] \quad 6.1$$

$$\Leftrightarrow \quad [M_y] + [M_{C_w}] = [M_R] + [M_{C_w}] + [M_{m_G}] + [M_{H_G}] \quad 6.2$$

Component balance

$$[M_{substrate}] = [y] = \begin{bmatrix} \overbrace{x}^{Solid} \end{bmatrix} + \begin{bmatrix} \overbrace{m_o}^{Water} \end{bmatrix} \quad 6.3$$

$$\left[M_{freshWater}\right] = \left[fw\right] = \left[\overbrace{M_{fw}}^{Water}\right] \quad 6.4$$

The cyclewater was assumed to contain no dissolved solids

$$\left[M_{rest}\right] = \left[R\right] = \left[\overbrace{a_1}^{solid}\right] + \left[\overbrace{b_1}^{Water}\right] \quad 6.5$$

$$\left[M_{cycleWater}\right] = \left[C_w\right] = \left[\overbrace{d}^{Solid}\right] + \left[\overbrace{w}^{Water}\right] + \left[\overbrace{b}^{Volatile\ Compound}\right] \quad 6.6$$

$$\left[M_{biogas}\right] = \left[M_G\right] = \left[M_{CH_4}\right] + \left[M_{CO_2}\right] + \left[M_{water\ vapour}\right] \quad 6.7$$

$$\left[M_{hydrolysisGas}\right] = \left[H_G\right] = \left[M_{CH_4}\right] + \left[M_{CO_2}\right] + \left[M_{water\ vapour}\right] \quad 6.8$$

NB: Cycle water is the effluent from the methane reactor and from an economic view point, it does not make sense to discard this liquid and go for fresh water from the tap. The same process water is used over and over and occasionally replenished with fresh water from the tap. Therefore, in the subsequent analysis, cycle water will mainly be used instead of fresh water.

6.1.2 Material flow in the batch hydrolysis reactor

The material flow in the hydrolysis reactor is presented in the flow diagram presented in figure 6.2.

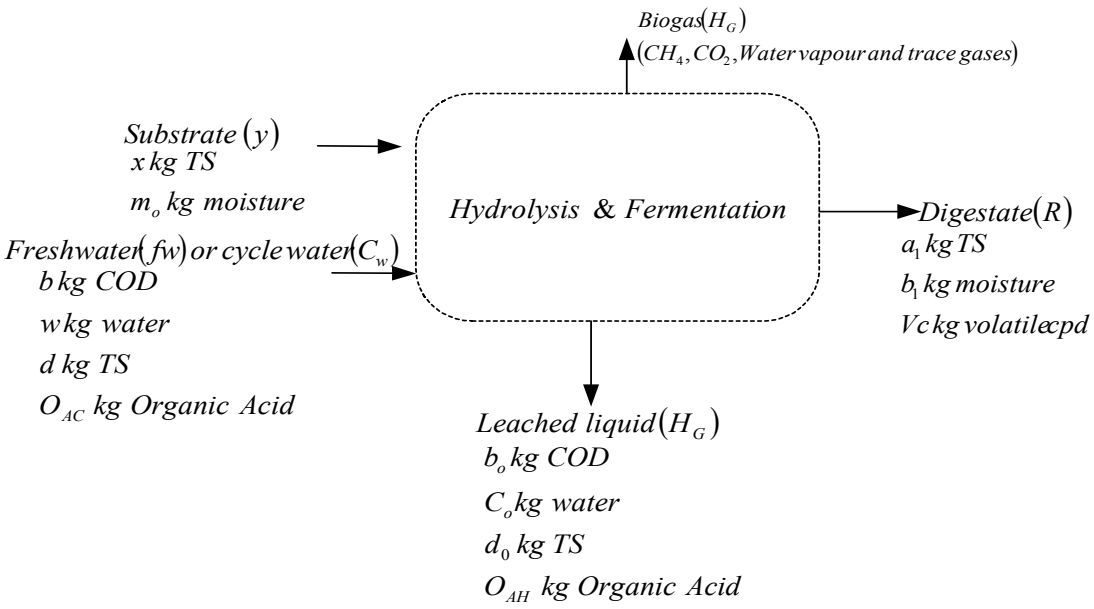


Figure 6.2. The flow of materials through the hydrolysis reactor.

Assumptions:

- COD, OA and TS of the cycle water are not neglected
- Traces of gas are neglected

Total mass balance

$$[M_{substrate}]+[M_{freshwater}]+[M_{cyclewater}]=[M_{rest}]+[M_{hydrolysisGas}]+[M_{hydrolysisLiquid}] \quad 6.9$$

Component balances

Recalling equations: 6.3, 6.6, 6.5, 6.8 for component balances of substrate (y), cyclewater (Cw), digestate (R), and hydrolysis gas (H_G) respectively.

$$[M_{hydrolysisLiquid}]=[H_L]=\begin{bmatrix}\overbrace{a}^{Solid}\end{bmatrix}+\begin{bmatrix}\overbrace{c_0}^{Water}\end{bmatrix}+\begin{bmatrix}\overbrace{b_o}^{VolatileCompound}\end{bmatrix} \quad 6.10$$

Assuming the water and the COD components are the main components of the hydrolysed liquid, then equations 6.11 and 6.12 holds.

$$[M_{cycleWater}]=[C_w]=\begin{bmatrix}\overbrace{w}^{Water}\end{bmatrix}+\begin{bmatrix}\overbrace{b}^{COD}\end{bmatrix} \quad 6.11$$

$$[M_{hydrolysisLiquid}]=[H_L]=\begin{bmatrix}\overbrace{c_0}^{Water}\end{bmatrix}+\begin{bmatrix}\overbrace{b_o}^{COD}\end{bmatrix} \quad 6.12$$

Therefore,

$$From\ equ\ (6.6)\ and\ (6.10)$$

$$[M_{hydrolysis\ liquid}]-\begin{bmatrix}\overbrace{M_{cycleLiquid}}^{Water}\end{bmatrix}=\begin{bmatrix}\overbrace{M_{hydrolysisLiquid}}^{COD}\end{bmatrix}-\begin{bmatrix}\overbrace{M_{cycleLiquid}}^{COD}\end{bmatrix} \quad 6.13$$

The actual COD of the leachate produced in the hydrolysis stage is given by equation 6.14, 6.15 and 6.16.

$$\begin{bmatrix}\overbrace{M_{Hydrolysis\ liquid}}^{Actual\ COD}\end{bmatrix}=\begin{bmatrix}\overbrace{M_{hydrolysis\ liquid}}^{COD}\end{bmatrix}-\begin{bmatrix}\overbrace{M_{cycle\ liquid}}^{COD}\end{bmatrix} \quad 6.14$$

$\Leftrightarrow$

$$\left[Mass\ of\ Actual\ COD_{hydrolysisLiquid}\right] = \left[\overbrace{M_{hydrolysisLiquid}}^{COD}\right] - \left[\overbrace{M_{cycleLiquid}}^{COD}\right] \quad 6.15$$

$\Leftrightarrow$

$$\left[H_{L\ Actual\ COD}\right] = \left[b_o\right] - \left[b\right] \quad 6.16$$

Also

The COD of the cycle water is function of its solids and the volatile compounds as shown in equation 6.17 and 6.18.

$$\left[\overbrace{M_{cycleWater}}^{COD}\right] = f\left(\langle\overbrace{M_{cycleWater}}^{Solid}\rangle + \langle\overbrace{M_{cycleWater}}^{VolatileCompound}\rangle\right) \quad 6.17$$

$\therefore$

$$\left[b\right] = f\left[d + volatile\ compounds\right] \quad 6.18$$

The degradation rate of the substrate material is computed according to equation 6.19

$$\frac{\left[\overbrace{M_{\deg raded}}^{Solid}\right]}{\left[\overbrace{M_{substrate}}^{Solid}\right]} = \frac{\left[x - a_1\right]}{x} = n = \quad Degradation\ Rate \quad 6.19$$

The leaching rate of the degradable material is obtained by equation 6.20

$$\frac{\left[\left[\overbrace{M_{hydrolysisLiquid}}^{COD}\right] - \left[\overbrace{M_{cycleWater}}^{COD}\right]\right]}{\left[\overbrace{M_{substrate}}^{Solid}\right]} = \frac{\left[H_{L\ Actual\ COD}\right]}{\left[x\right]} = V\ = Leaching\ \ Rate \quad 6.20$$

The parameter Z in equation 6.21 is a ratio of the actual COD of the hydrolysed leachate to the substrate degraded. The magnitude of the parameter is dependent on the extent of methanogenesis taking place in the hydrolysis stage. The more biogas produced from this stage, the less the COD will be delivered to the methane reactor.

$$\frac{\left[\left[\overbrace{M_{hydrolysisLiquid}}^{COD}\right]-\left[\overbrace{M_{cycleWater}}^{COD}\right]\right]}{\left[\left[\overbrace{M_{substrate}}^{Solid}\right]-\left[\overbrace{M_{substrate}}^{Rest}\right]\right]}=\frac{\left[H_{L\ Actual\ COD}\right]}{\left[M_{substrate\ degraded}\right]}=Z=f\left(Gas\ prodtn\ in\ hydrolysis\right) \qquad 6.21$$

The quantity of COD that is converted to organic acid is referred to as hydrolysis given by equation 6.22

$$\frac{\left[\left[\overbrace{M_{hydrolysisLiquid}}^{Organic\ Acid}\right]-\left[\overbrace{M_{cycleWater}}^{Organic\ Acid}\right]\right]}{\left[\left[\overbrace{M_{hydrolysisLiquid}}^{COD}\right]-\left[\overbrace{M_{cycleWater}}^{COD}\right]\right]}=\frac{\left[H_{L\ Actual\ OA}\right]}{\left[H_{L\ Actual\ COD}\right]}=\frac{\left[O_{AH}-O_{AC}\right]}{\left[b_o-b\right]}=Hydrolysis \qquad 6.22$$

6.1.3 Material flow in the methane reactor

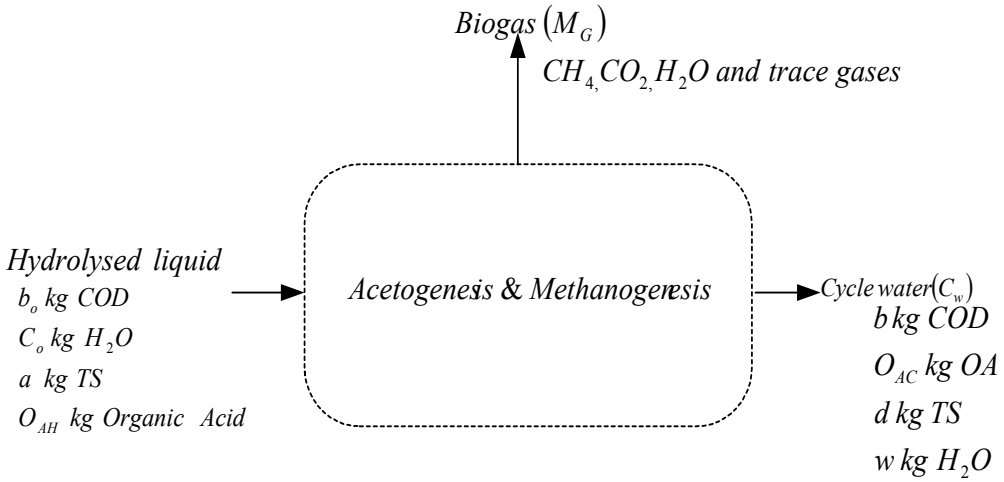


Figure 6.3. Material flow through the methane reactor.

<u>Total mass balance around the hydrolysis</u>

The overall material flow through the methane reactor is given by equation 6.24

$$\left[M_{hydrolysisLiquid}\right]=\left[M_{cycleWater}\right]+\left[M_{wasteWater}\right]+\left[M_{Biogas}\right] \qquad 6.23$$

$\Leftrightarrow$

$$\left[H_L\right]=\left[M_{cw}\right]+\left[M_{fw}\right]+\left[Mm_G\right] \qquad 6.24$$

Component balance

The quality of the hydrolysed COD going to the methane reactor is a function of the solid content and the volatile compound as expressed by equation 6.25.

$$\left[M_{hydrolysisLiquid}\right]=\left[\overbrace{M_{hydrolysisLiquid}}^{Water}\right]+\left[\overbrace{M_{hydrolysisLiquid}}^{COD}\right]=f\left(\left[\overbrace{M_{hydrolysisLiquid}}^{Solid}\right]+\left[\overbrace{M_{hydrolysisLiquid}}^{VolatileCompound}\right]\right) \quad 6.25$$

$\Leftrightarrow$

$$\left[H_L\right]=\left[c_o\right]+\left[b_o\right]=f\left(d_o+volatile\ compds\right) \quad 6.26$$

The mass of the cycle water is related to it contents by the equations 6.27 and 6.28

$$\left[M_{cycleWater}\right]=\left[\overbrace{M_{cycleWater}}^{Water}\right]+\left[\overbrace{M_{cycleWater}}^{COD}\right] \quad 6.27$$

$\Leftrightarrow$

$$\left[M_{cw}\right]=\left[w\right]+\left[b\right] \quad 6.28$$

Seldomly fresh water is used. However, its component balance is given by equations 6.29 and 6.30.

$$\left[M_{freshWater}\right]=\left[\overbrace{M_{freshWater}}^{Water}\right]+\left[\overbrace{M_{freshWater}}^{COD}\right] \quad 6.29$$

$\Leftrightarrow$

$$\left[M_{fw}\right]=\left[w\right]+\left[b\right] \quad 6.30$$

The balance for biogas produced in the methane reactor is given by equations 6.31 and 6.32.

$$\left[M_{mG}\right]=\left[\overbrace{M_{biogas}}^{Gas}\right]+\left[\overbrace{M_{biogas}}^{Water}\right] \quad 6.31$$

$\Leftrightarrow$

$$\left[M_{mG}\right]=\left[M_{CH_4}\right]+\left[M_{CO_2}\right]+\left[M_{H_2O\ Vapour}\right] \quad 6.32$$

The parameter Φ as shown in equation 6.33 and 6.34 shows the ratio of the biogas to the actual COD coming from the hydrolysis reactor. The more the ratio approaches unity the higher the conversion of the COD to biogas.

$$\frac{\left[\overbrace{M_{biogas}}^{Gas}\right]}{\left[\left[\overbrace{M_{hydrolysisLiquid}}^{COD}\right]-\left[\overbrace{M_{cycleWater}}^{COD}\right]-\left[\overbrace{M_{wasteWater}}^{COD}\right]\right]}=\Phi=\frac{\left[\overbrace{M_{biogas}}^{Gas}\right]}{\left[\left[\overbrace{M_{hydrolysisLiquid}}^{COD}\right]-\left[\overbrace{M_{cycleWater}}^{COD}\right]\right]} \quad 6.32$$

$\Leftrightarrow$

$$\frac{\left[M_{mG}\right]}{\left[M_{H_L Actual\ COD}\right]}=\Phi=\frac{\left[M_{mG}\right]}{\left[M_{H_L Actual\ COD}\right]} \quad 6.33$$

Also, the degree of biomethanization is presented in equation 6.34. The value of the ratio indicates the degree of fermentation and for that matter is proportional to the extent of biogas production in the methane reactor at favourable conditions.

$$\frac{\left[M_{H_L Actual\ Organic\ Acid}\right]}{\left[M_{H_L Actual\ COD}\right]}=\Psi=\deg ree\ of\ biomethanization \quad 6.34$$

The parameter Y is called the gas production rate and is the produced biogas/reactor volume ratio, in a given time.

$$\frac{\left[m^3 biogas\right]}{\left[m^3\ \mathrm{Re}actor * d\right]}=\mathrm{Y} \quad 6.35$$

The analysis and evaluation of results are presented in a chronological order in the following sections.

6.2 Characteristics of the simulated waste

The simulated waste was mainly organic degradable material. Part of the non-degradable fraction consisted of polyethylene bags, cans, glass, sand and others. Source separation was not done since the main emphasis was on pre-treatment of the unsorted bulk waste. About 20 kg (wet weight) of the simulated waste was fermented in each experimental run.

Figure 6.4 shows the basic characteristics of the derived waste used throughout the study which reflects the average percentage values of the different materials present in the simulated input waste.

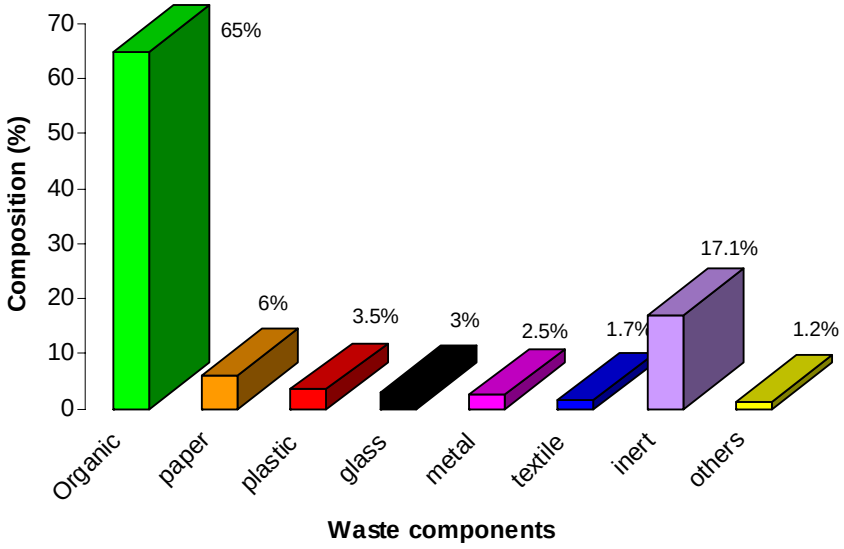


Figure 6.4. Composition of the simulated waste

The cumulative average moisture content of the simulated UMSW was 77% on wet basis. As indicated by the moisture content it is a highly wet material and also due to its biowaste source (fruit and vegetables) it contains highly biodegradable fraction. The high moisture content of the waste as shown in table 6.1 along with its high organic fraction is attractive to process the waste in anaerobic digestion process.

Table 6.1. Characteristics of the simulated waste.

Parameters	Unit	Simulated waste	
		Range	Average
Moisture	%	74-79	77
Total solid	%	21-26	22
Volatile solid	%	61-70	65
Carbon	%	27-74	53
Nitrogen	%	1.3-2.1	1.6
C/N Ratio	-	17-50	32

6.3 Effect of water flow rate (dilution) on leaching of particulate matter

6.3.1 Solid degradation in the hydrolysis phase

The substrate was very dry, therefore, it was diluted in the hydrolysis reactor with fresh water or effluent from the methane reactor. Dilution was achieved by adding specific amount of water per kg of input feed material as already indicated in the previous chapter.

Due to the high heterogeneity of the waste used in the experiment, the internal arrangement of individual material is very variable within the reactor. Hence, in order to ascertain the extent of removal of particulate matter from the matrix of the UMSW, the extent of particulate matter removal was characterized by leaching rate. Leaching rate was one of the parameters used to measure the efficiency of the degradation in the hydrolytic reactor. From the COD mass balance around the hydrolytic reactor, leaching rate (V) is given according to equation 6.20 shown below,

$$Leaching\ Rate\,(V) = \frac{\left[H_{L\ Actual\ COD}\right]}{[X]} * 100\% \qquad 6.20$$

Where:

$H_{L\ Actual\ COD}$ is the total actual COD produced during the hydrolysis in kgCOD/L effluent

X is the dry mass of organic total solids of the input solid material of the hydrolysis reactor as kg OTS.

Figure 6.5 shows the influence of flow rate on leaching.

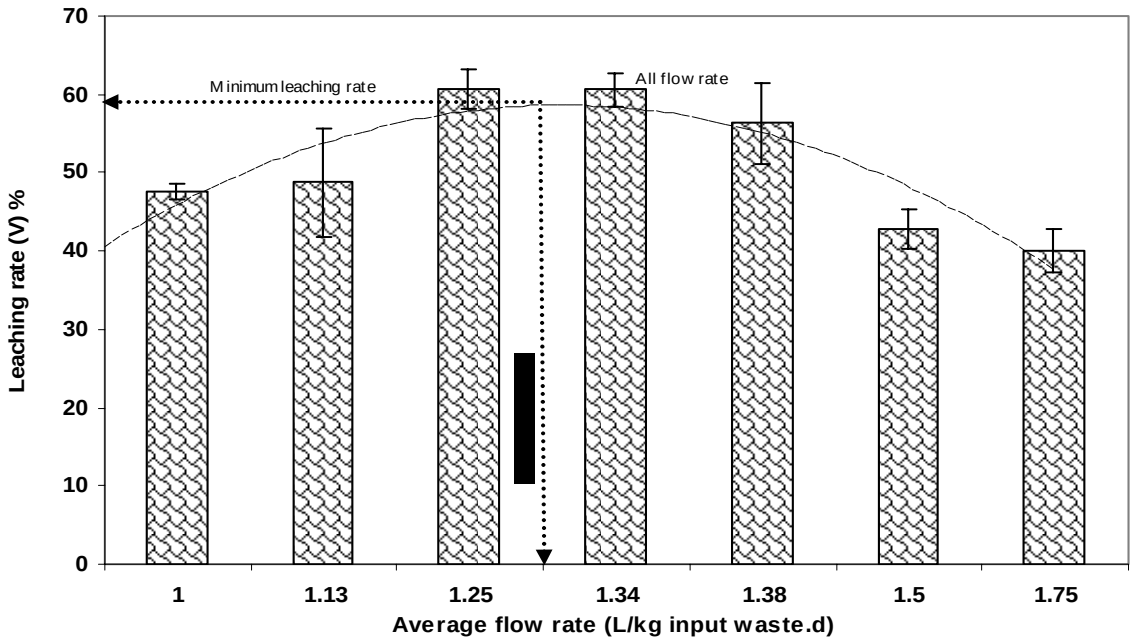


Figure 6.5. Bar distribution of the leaching rate at various flow rate regimes (dilution).

Twardowska et al. (2004) reported that leaching behaviour of constituents from solid waste is dependent on the nature of the waste (degradable organic matter) and the applied operational parameters such as liquid to solid ratio referred to here as water flow rate regime (continuous percolation of the waste with defined quantity of water per unit mass, which corresponds to a specific HRT-contact time) and pH.

On the average, 51±8% leaching rate of particulate matter was achieved. It ranged from a minimum of 42.8±2.6% to a maximum of 60.8±2.5% as shown in a bar distribution of leaching rate in figure 6.5. From figure 6.5, it is seen that, leaching rate was influenced or affected by the flow rate regime applied i.e. extent of dilution on COD removal per unit organic total solid. The trend obtained shows lower leaching rate of 47.6±1.1% and 42.8±2.6% was observed at an extremely lower and higher flow rate regimes respectively. The relatively lower performance observed for the high and low flow rates (1.5 and 1.75 l/kg input waste.d) could be attributed to the possible wash-out of the acidifiers at a considerable high flow rate corresponding to HRT of 0.35 days and the later could be due to inadequate dilution and percolation at low flow rate corresponding to HRT of 0.41 days. High delivery of liquid (short HRT) will result in short contact time between the bacteria and the substrate, thus organic material will not be fully degraded resulting in possible microbial wash out.

Low delivery of liquid (high HRT) will ensure long contact time between the bacteria and the organic substrate resulting in high substrate degradation especially in the case of the methane reactor but longer digestion time. In addition, long contact time could affect the hydrolytic bacteria if the pH is too low, i.e. inhibition effect. The efficiency not only depends on the HRT, but also the feedstock composition and reactor temperature. Hofenk et al, (1984) confirmed that at a higher water to waste ratio, the concentration of the solubilized material (e.g. OA, COD etc) becomes unnecessarily low (i.e. < 5 g COD/l). On the contrary, for lower water to waste ratio, solubilized effluents from the hydrolytic reactor may have COD concentrations ≥50 gCOD/l and a pH as low as 4.2.

Nevertheless, degradation rate (figure 6.6) of the solid material was found to follow similar trend as leaching rate (illustrated in figure 6.5). Similarly, the explanation leading to the trend obtained for the leaching rate observed in figure 6.5, holds for degradation rate.

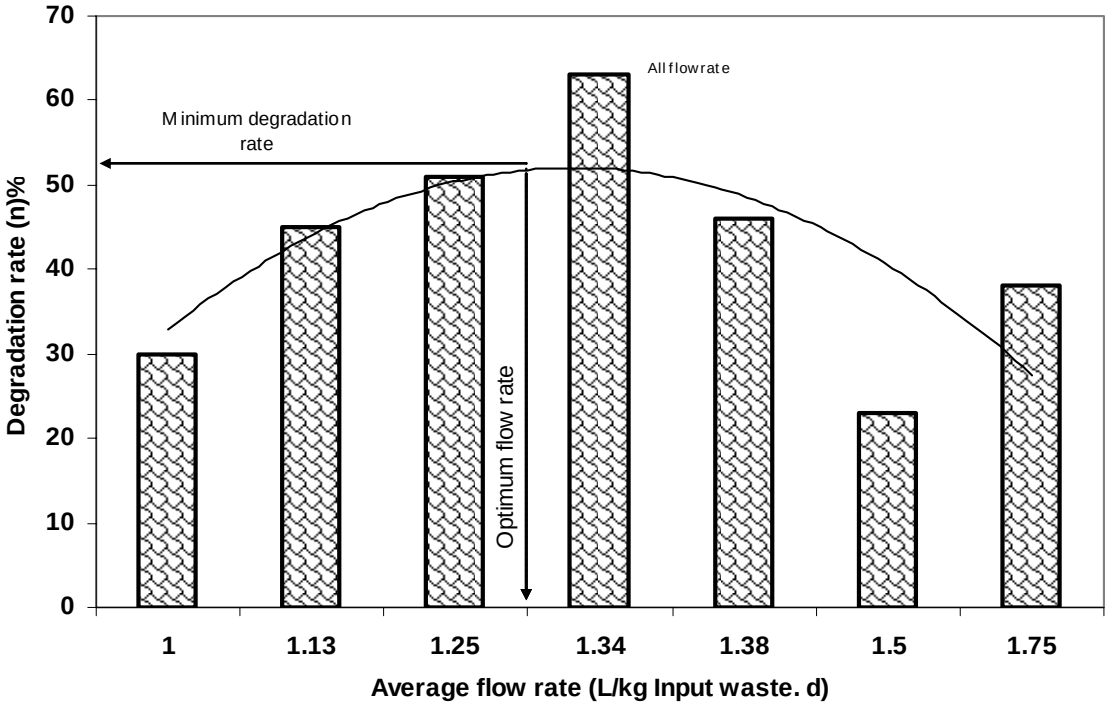


Figure 6.6. Bar distribution of the degradation rate at various flow rate regimes (dilution).

At high and low flow rate regimes, degradation rate is lowered. A discrepancy was observed at a flow rate of 1.75 l/kg input waste.d in figure 6.6. The explanation of this anomaly is that, applying high flow rate of process water, may have washed away most of the available loose material instead of it being consumed and broken down by the hydrolytic microorganisms.

On the average, 42.3±13.2% degradation rate was obtained, with a minimum of 23% and a maximum of 63%. For decision making, a minimum leaching rate of 59% could be obtained at a water flow rate range of 1.25 – 1.34 l/kg input waste.d. (figure 6.5). However, the same water flow rate range of 1.25 – 1.34 l/kg input water.d would result in a minimum degradation rate of 52%.

In summary, using flow rate (dilution) as factor, the null hypothesis (no effect) for COD leaching per unit organic total solid digested could be rejected according to the trend line criteria shown in the bar distribution in figure 6.5. From this type of analysis it is obvious that COD production is influenced by dilution.

A linear regression of specific COD production as a function of flow rate is presented in figure 6.7.

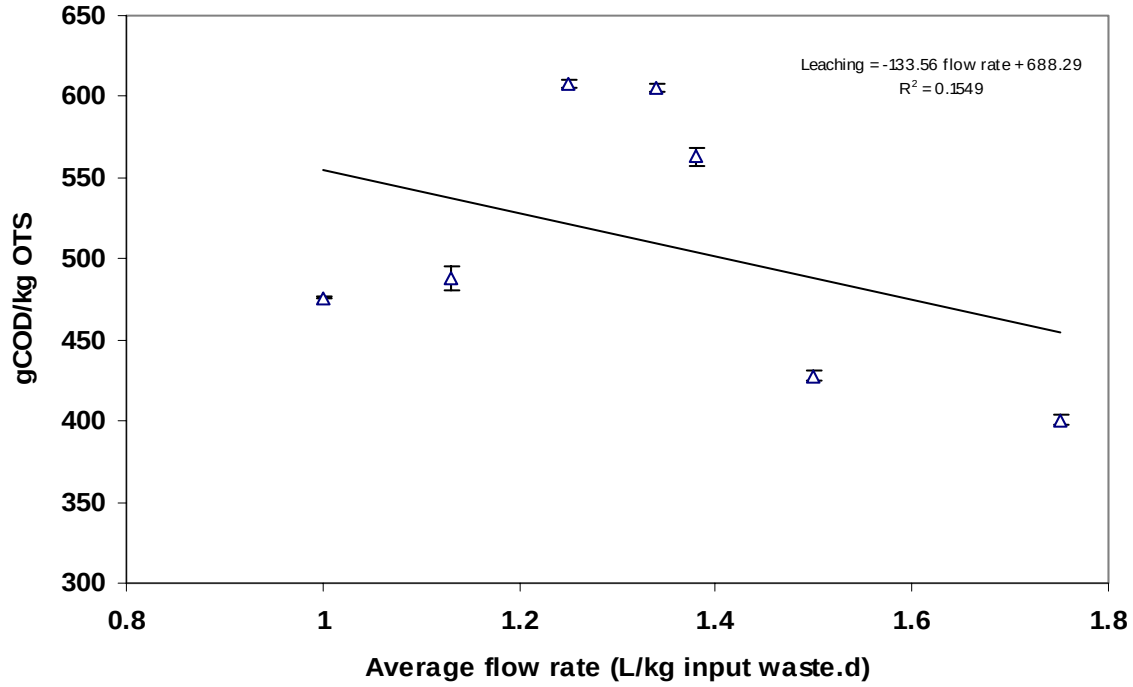


Figure 6.7. Average leaching rate with respect to flow rate regime.

From regression analysis (Figure 6.7), water flow rate (dilution) predicts only 15% of the trend being observed in Figure 6.7. This implies that 85% of the influence comes from other potential factors such as the quality of the waste, temperature and pH. At 99% confidence interval, the values obtained for the leaching rate were tested about their validity within this interval range (figure 6.8).

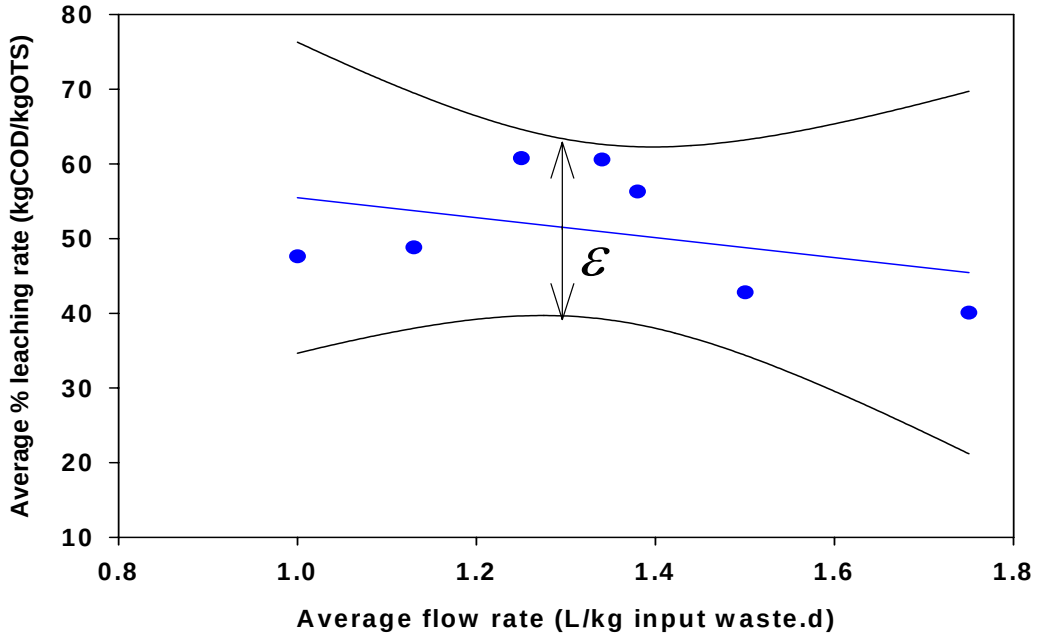


Figure 6.8. Average leaching rate within a confidence interval.

$$Confidence\ \ region\ ,\ \varepsilon = \hat{y} \pm t_{\alpha}.s_{\hat{y}}$$
$$\alpha = significan\ t\ level\ = 0.01$$
$$\varepsilon = 1 - \alpha\ confidence\ \ level\ = 99\%$$
$$s_{\hat{y}} = s\tan dard\ \ deviation\ = \sqrt{s_{\hat{y}}{}^{2}}.\frac{(x-\bar{x})^{2}}{n\sum(x)^{2}}$$

The relationship between flow rate regime and HRT as a function of leaching rate and hydrolysis rate constant was not a linear one (figure 6.9) but agrees more with experimental results.

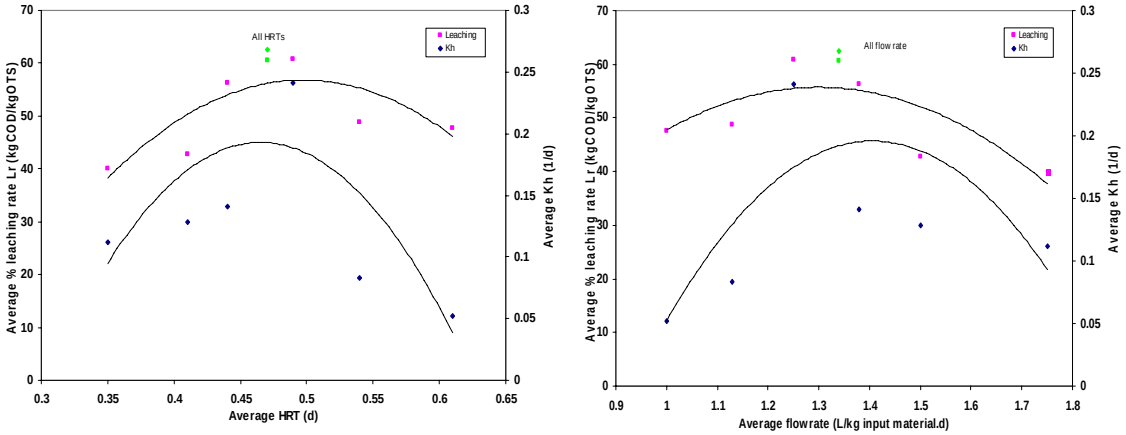


Figure 6.9. Effect of flow rate regime and HRT on leaching rate and hydrolysis rate constant**.**

Both leaching and hydrolysis rate constant decreases at a lower and a higher water flow rate regimes. A similar pattern is followed by leaching rate and hydrolysis rate constant with HRT. Higher leaching rate and hydrolysis rate constant were found to be between HRT of 11 and 12 hours. According to the studies carried out by Hofenk et al. (1984), it was observed that HRT between 12 and 24 hours, or similarly between 2 and 1 volumes of water of the hydrolytic reactor per day, is sufficient for an optimal, non-inhibited hydrolysis. The organic matter content variation with flow rate regime during the degradation is presented in figure 6.10.

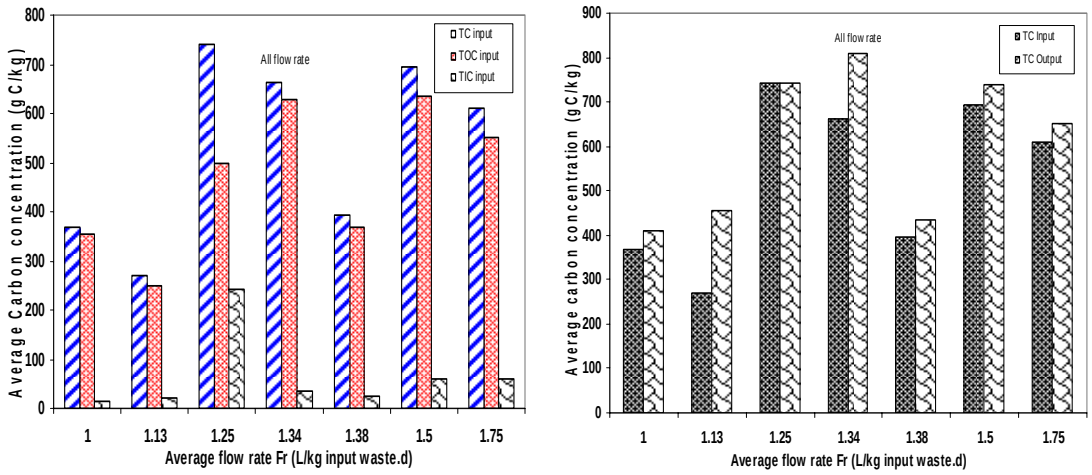


Figure 6.10. Effect of flow rate on carbon leaching.

The content of organic matter is a key parameter measured in most of anaerobic digestion studies. The organic matter varies widely between different fresh materials (Lens et al., 2004) and this tend to decrease during anaerobic digestion as the organic matter is being utilized by the microorganisms. Furthermore, the measurement of TOC helps to establish the C/N ratio of the input material. The average concentration of total carbon in the input waste before digestion was found to be 534±189 gC/kg, having a range of 269–742 gC/kg. The average total organic carbon content before digestion was found to be 469±149 gC/kg dry sample with a range of 247 to 636 gC/kg dry sample.

The average total organic carbon was found to constitute 89±10 % of the total carbon content of the input material. But after digestion, the total organic carbon was found to constitute 94±6% of the output total carbon of the waste, which implies slight increase with respect to the output total carbon content as shown in figure 6.11.

The reason for the increase in total carbon after digestion is due to increase in concentrations of both organic and inorganic carbon that do not contribute to the anaerobic digestion.

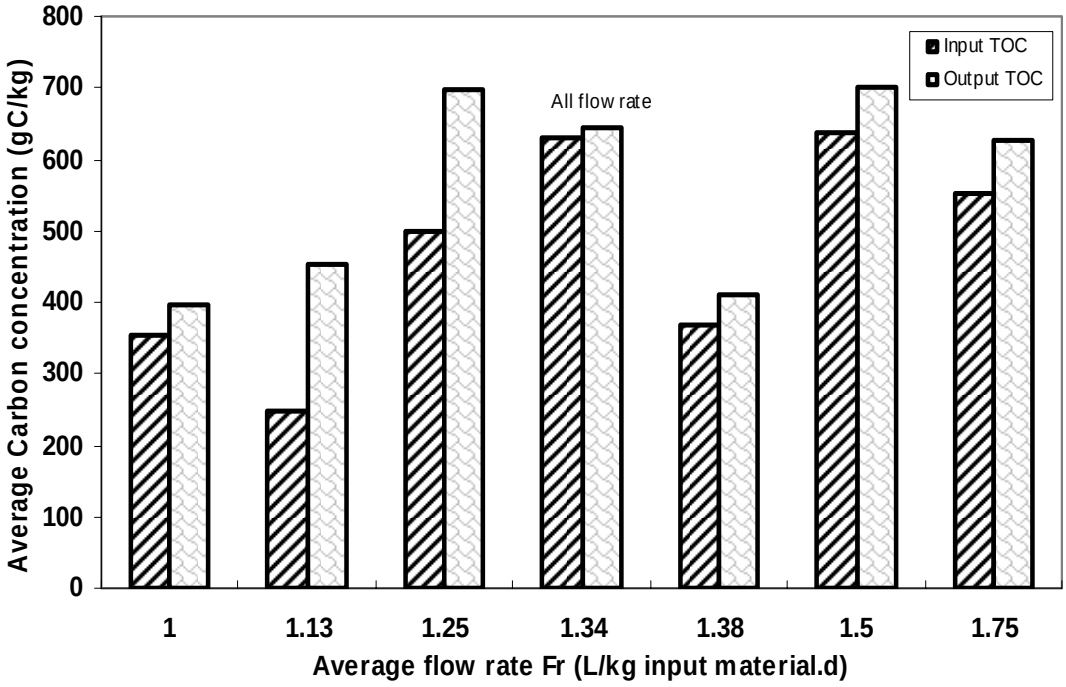


Figure 6.11. Average carbon variation before and after digestion

Similarly, there was also a slight increase in the total organic carbon after digestion.

The C/N ratio decreases during fermentation according to Lens et al. (2004). This was confirmed in the study. The profiles of the variations of the C/N ratios and the TON across the tests are presented in figure 6.12.

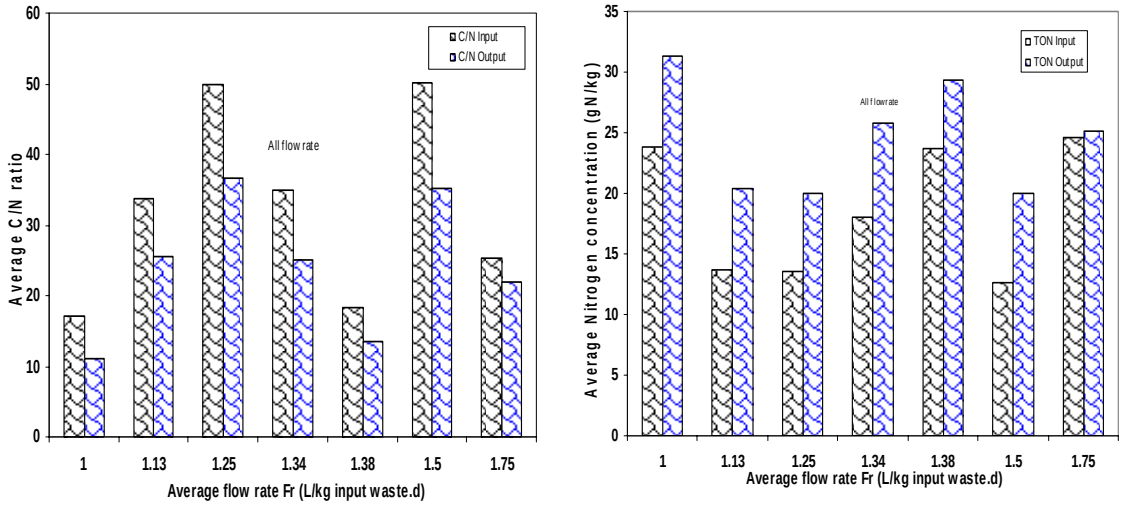


Figure 6.12. C/N ratio and TON of the input and output waste.

On average C/N ratio reduction of 27% was observed after digestion. The reduction in the C/N ratio could be due to the rapid degradation of organic matter, mainly cellulose and other readily available carbon, and the consequent volatilization of organic to CO_2. Microorganisms consume carbon for energy and growth and nitrogen is essential for their protein production and reproduction.

This reduction in the C/N ratio after 10 days indicates the maximum use of available nutrients in the waste, which otherwise could pose a potential threat if not treated before disposal or landfilling.

The C/N can not be used seriously as stability indicator, as the ratio does not account for only biodegradable forms of carbon and nitrogen but also for non-biodegradable fractions like lignin. Nevertheless the initial values of the raw waste before digestion put the entire process in a safe position from ammonia inhibition.

There was an average of 36 ±19 % increase of TON after digestion for all the experiments ranging from a minimum of 2 % to a maximum of 58 %. The wide variation is not a surprise since the C/N ratio and the nutrient content of UMSW vary significantly depending on the compositions of the individual fractions of UMSW. The different organic fractions (food waste, yard waste, paper, newspaper, etc.) have different C/N ratios (Mata-Alverez, 2004). Lissen et al. (2001) reported that by adding fresh water to high-solids waste, the ammonia inhibition effect could be mitigated. Furthermore, Lissen et al. (2001) cited that for solid wastes with a C/N ratio above 20, the ammonia inhibition effect can be compensated by the dilution effect of water which lowers the concentration of potential inhibitors. For high solids digesters, an optimum C/N ratio for methane production with no adverse effect on the performance was found to be in the range of 25 to 30, based on the biodegradable carbon. Therefore, Carbon-to-nitrogen (C/N) ratio of 25, was considered acceptable to sustain anaerobic metabolism with no nutrients being added to the UMSW. Vieitez et al. (2000) reported C/N ratio of 25 of simulated waste similar to the feed applied in this study was acceptable and operated well without any inhibition during the biomethanization process.

The pattern of reduction of the TON values after digestion does not follow any pattern with the water flow rate regime (dilution). It can be concluded that owing to the fluctuations in the composition of biowaste, a correlation between the water flow rate regimes on total organic nitrogen and C/N ratio changes cannot be discerned. Christ et al. (1999) experimenting with the two stage AD of OFMSW also observed a similar situation as a result of non homogeneity of substrates.

6.3.2 Liquid phase of the hydrolysis stage

The profiles of COD, OA VOS and TS with time are presented in figure 6.13. In all the profiles presented, it was observed that there was spontaneous acidification of the fresh waste within two days after the start of the experiment.

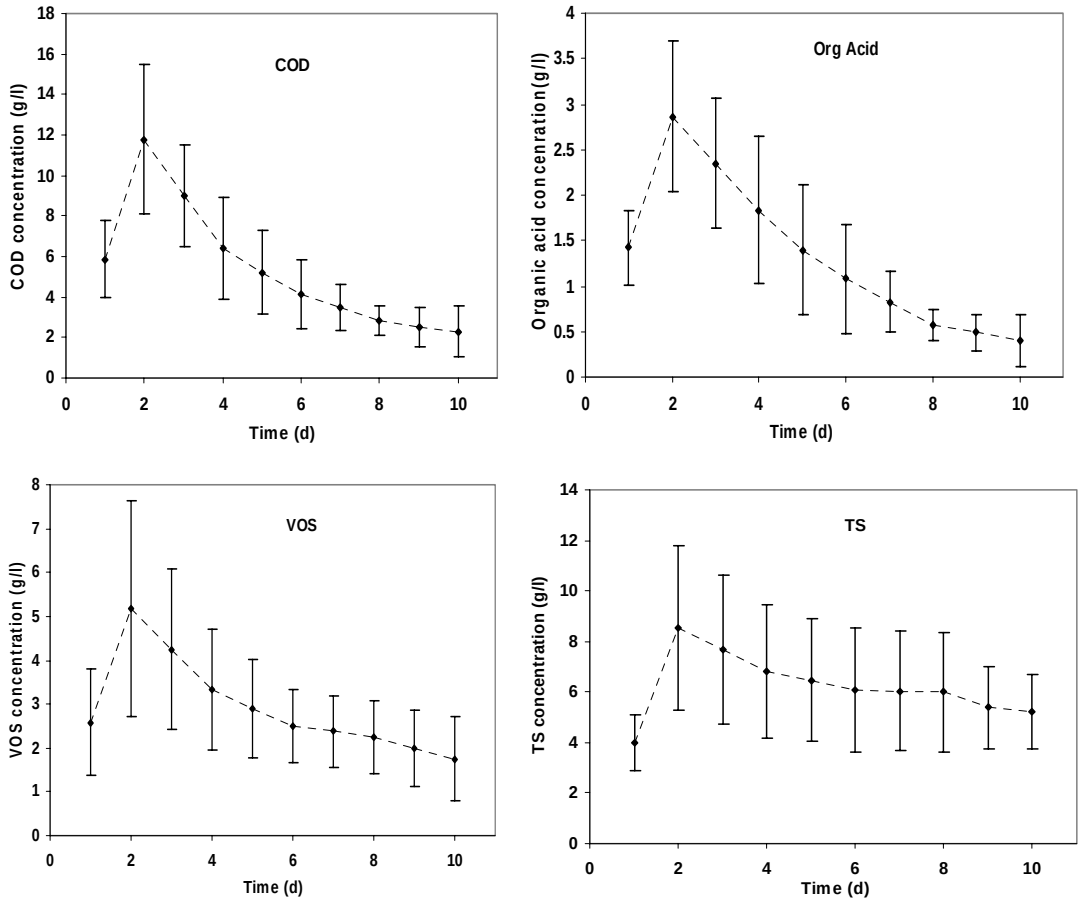


Figure 6.13. Average values with their standard deviation of the main leachate parameters of the hydrolytic process liquid. In all cases, the old numbered day's values are interpolated.

Dissolved material as COD rapidly increased up to 50 % (from 5.8±1.9 to 11.77±3.7g/l) for the first two days and then decreased continuously to lower values (2.3±1.3g/l). Similarly, OA,TS and VOS concentrations increased at the beginning of the fermentation and then decrease to the end of the hydrolysis in a similar fashion. Pavan et al. (2000) confirms this fact by adding that acidogenic conditions were quickly removed in two days during hydrolysis of fruit and vegetable waste. The odd day's values (e.g.1,3,5,7 and 9 day) were obtained by averaging the day before and the day after values. This phenomenon or approach might have over or underestimated the odd days values slightly.

The sharp increases of soluble substances at the beginning of the hydrolytic process is dependent on the characteristics of the substrate. Soluble carbohydrates in aqueous fraction are easily biodegradable by microorganisms which support the fact that soluble carbohydrates are quickly consumed at the beginning of fermentation (Lens, 2004). Mirion et al. (2000) observed that the strongest increase in hydrolysis of total COD could be observed at solid retention time of 3 days. The significant increase of COD in the generated leachate indicates an active hydrolytic phase. This was confirmed in this experiment of having a maximum hydrolysis yield obtained by 2 days of the hydrolysis operation. It means that an active hydrolytic phase occurs within the first 2 days of operation.

It was observed that the variation in the first 2 days for the production of OA and VOS was pronounced of having almost 30% and 50% respectively of COD equivalent produced. This fact is illustrated in figure 6.14 below. The high VOS value could result from additional VOS due to slurry washout in the process water coming from the effluent of the methane reactor.

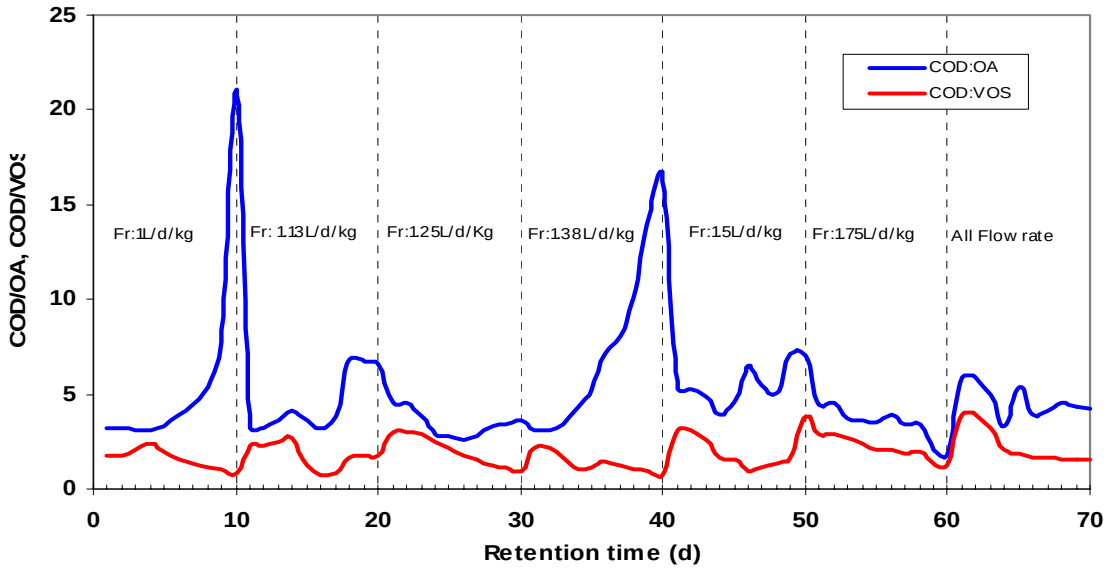


Figure 6.14. The ratio of COD, OA and VOS of the hydrolytic reactor for the various test conducted. The broken vertical lines indicates the beginning of each batch test.

A regression analysis is presented below in figure 6.15 about the main components of the COD produced during hydrolysis. It is seen from figure 6.15 that the organic acid production is the main component of the COD concentration.

The regression analysis shows that OA represent about 74% of the COD while the VOS predicts 60%.

Traverso et al. (2000) observed having almost all of the solubilized organic matter being converted to organic acid in a mesophilic acidogenic treatment of vegetable and fruit mixture at HRT greater than 6 days.

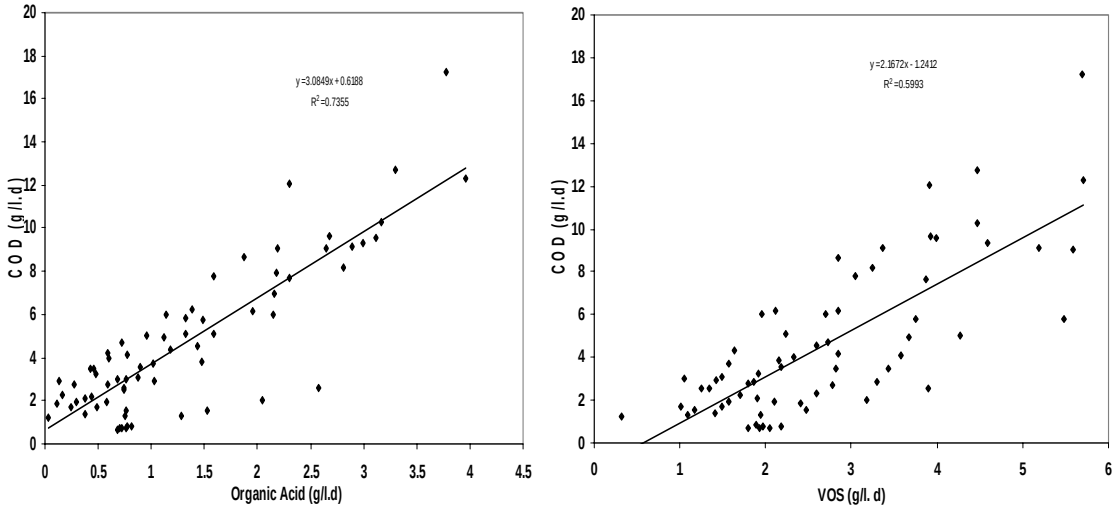


Figure 6.15. The main constituent of the leached COD in the hydrolysis reactor.

It is very important to mention that the hydrolysis operation is crucial for early waste volume reduction and degradation. Since the main objective of the hydrolysis stage is to remove organic fraction as leachate to be delivered to the methane phase, 0.5 days of hydrolysis retention time could be good enough. Though the average contribution of OA to COD is high in the hydrolytic reactor, it suffers high variations of its fermented products with time in the buffer tank, as shown in figure 6.16 below.

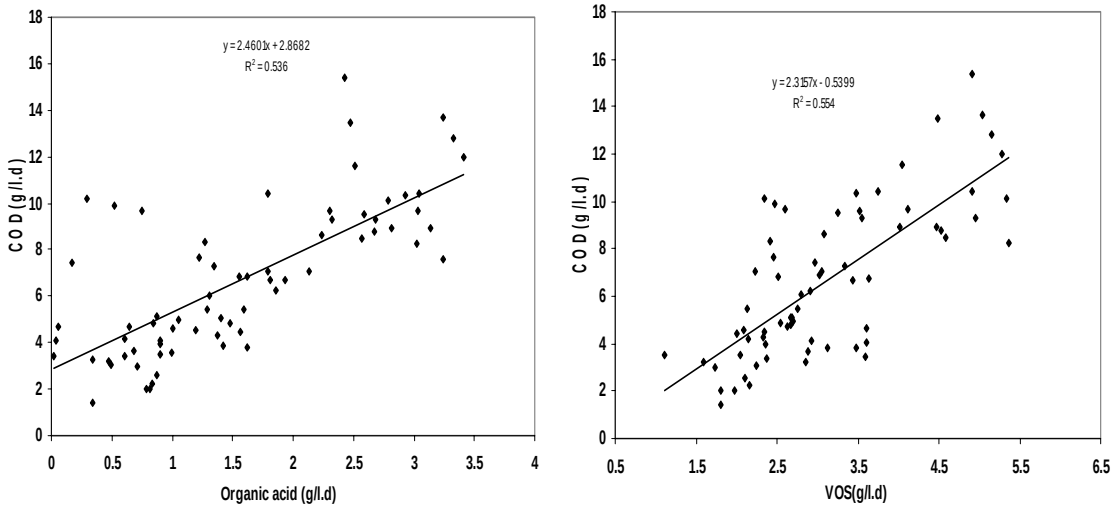


Figure 6.16. Organic acid and VOS as main contributors to the COD in the buffer tank.

pH and hydrolysis. pH on the other hand shows an obvious increase in values throughout the entire fermentation period. Figure 6.17 shows the evolution of pH in the reactor presented as average with one standard deviation without pH control.

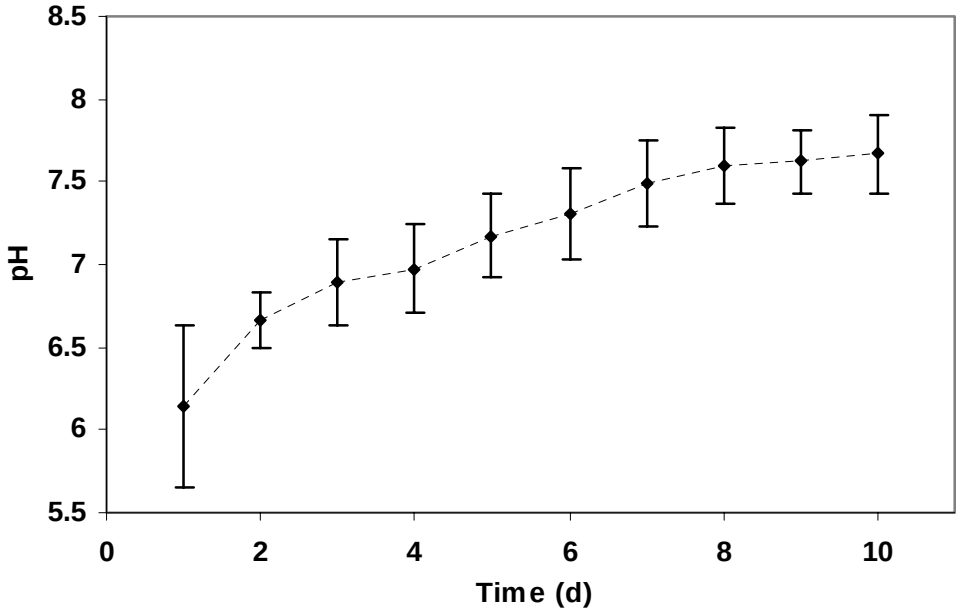


Figure 6.17. Average pH values with standard deviation during hydrolysis for the entire test.

Lower pH values (mean value of 6.1±0.49 and a corresponding value of 6.75±0.62 in the buffer) were observed during the first day of the hydrolysis when most of the easily degradable material are being degraded, but rose steadily to the end of the test. A minimum of 4.9 and a maximum of 7.9 were observed. The overall average pH for the entire experiment carried out was 7.14±0.55, a minimum of 6.1±0.49 and maximum of 7.7±0.24 were observed.

Dinamarca et al, (2003) reported pH ranges between 6.5 and 8.2 during the hydrolytic treatment of organic fraction of urban waste in a two stage process. Kübler et al. (1994) observed that the growth of hydrolytic microorganisms and the activity of their hydrolytic enzymes depends on pH. He further cited that under mesophilic conditions the pH for optimum growth of the cellulolytic bacterium *clostridium cellulovorans* is 7.0. The optimum conditions for the activity of the cellulose complex from *cellulomonas* range from pH 6.5 to 7 for the different enzymes.

Due to the operation mode of the process, it was possible to control both pH and TS content in the hydrolysis reactor. The pH inside the hydrolysis reactor was controlled by both the intra recirculation of hydrolysis content to the solid/liquid separation. Secondly, the TS contents in the hydrolysis is adjusted by the ratio of the recycled methane reactor effluent to liquid phase produced by solid/liquid separation.

Therefore, the trend of the pH values obtained in the study indicate that for the hydrolytic-acidogenic stage of the anaerobic digestion of the UMSW, it is not necessary to control the pH, as the reactor remains stable without the need for alkali or acid as buffer. Further test is required to prove this hypothesis.

It was observed that the mean pH values of the buffer was 10% higher than that of the hydrolyzed liquid. The general increase of pH in the buffer tank could be due to dilution. Also, determining the controlling factors of the pH in the hydrolytic reactor, recycling of the methane reactor effluent increases the buffer capacity in the hydrolysis stage. Kübler et al. (1994) confirmed this fact by emphasizing that resuspending the hydrolytic reactor with the methane reactor effluent increases the buffer capacity. As illustrated in table 6.2a-6.2g, salinity of the treated effluent from the methane reactor is always high compared to that of the influent liquid. This could be an indication of high presence of salts and probably high alkalinity.

On the contrary, the characteristics of the organic acid production accounts for the lower pH values during hydrolysis. During acidogenic phase, pH sharply decreases where as organic acid and BOD increases. When organic acid increases pH starts to decrease. From this relationship, pH and H^+ can be estimated as follows;

$$\frac{dpH}{dt} = -e\left(\frac{dOA}{dt}\right) \qquad if \quad \frac{dOA}{dt} \le 0$$

$$\frac{dpH}{dt} = -f\left(\frac{dOA}{dt}\right) \qquad if \quad \frac{dOA}{dt} > 0$$

$$pH = -\log\left(H^+\right)$$

Where e, f *are emperical cons* tan *ts*; *and OA is the organic acid*

Therefore, it can be concluded that, organic acid and the salinity could be the main controlling factors of the pH during hydrolysis. The variation of pH and conductivity of both the hydrolysis and buffer are presented in figure 6.18.

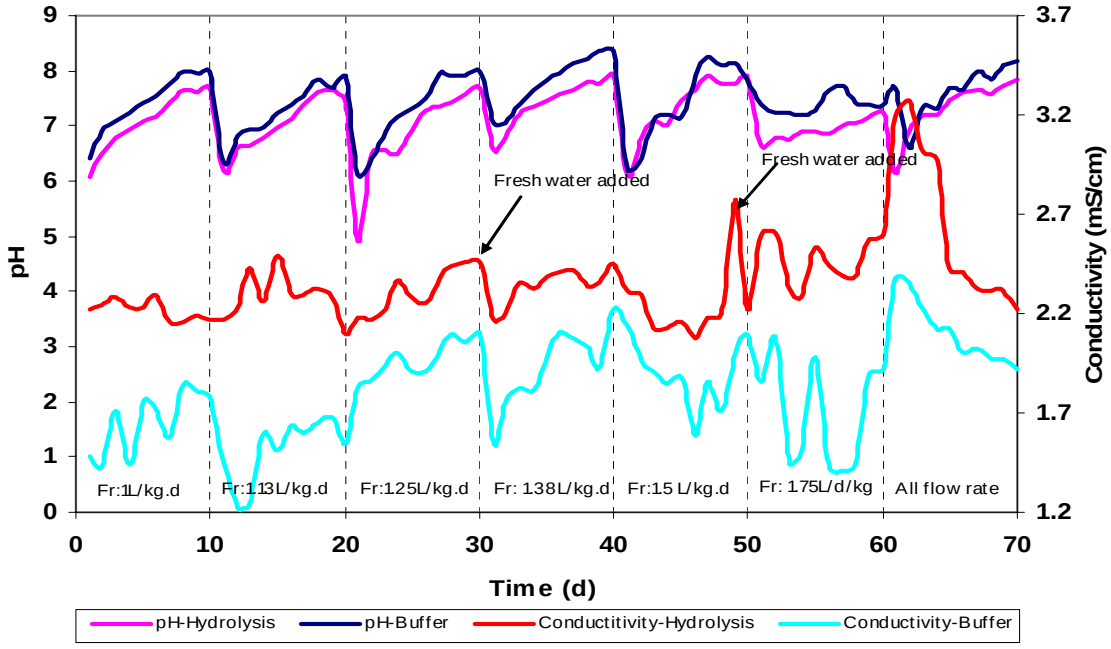


Figure 6.18. pH and conductivity variation in the hydrolysis and the methane reactors as a function of operation time.

Due to losses of process water from spillage, evaporation and frequent valve blockage, occasionally there is insufficient pumping of influent liquid from the buffer to the methane reactor resulting in a shortage of liquid in the methane effluent tank. Consequently this leads to a shortage of cycle water or effluent required to be pumped into the hydrolytic reactor for that day or in subsequent days; therefore an additional fresh water was required. As indicated in figure 6.18, additional 10 and 15 litres respectively of fresh water were added to the effluent liquid tank of the methane reactor on two occasions. The addition of the fresh water causes a decrease (dilution effect) in the conductivity of the hydrolysis liquid as indicated in the same figure 6.18.

The sum effect of the organic acid and conductivity on pH was studied by regression analysis shown in figure 6.19.

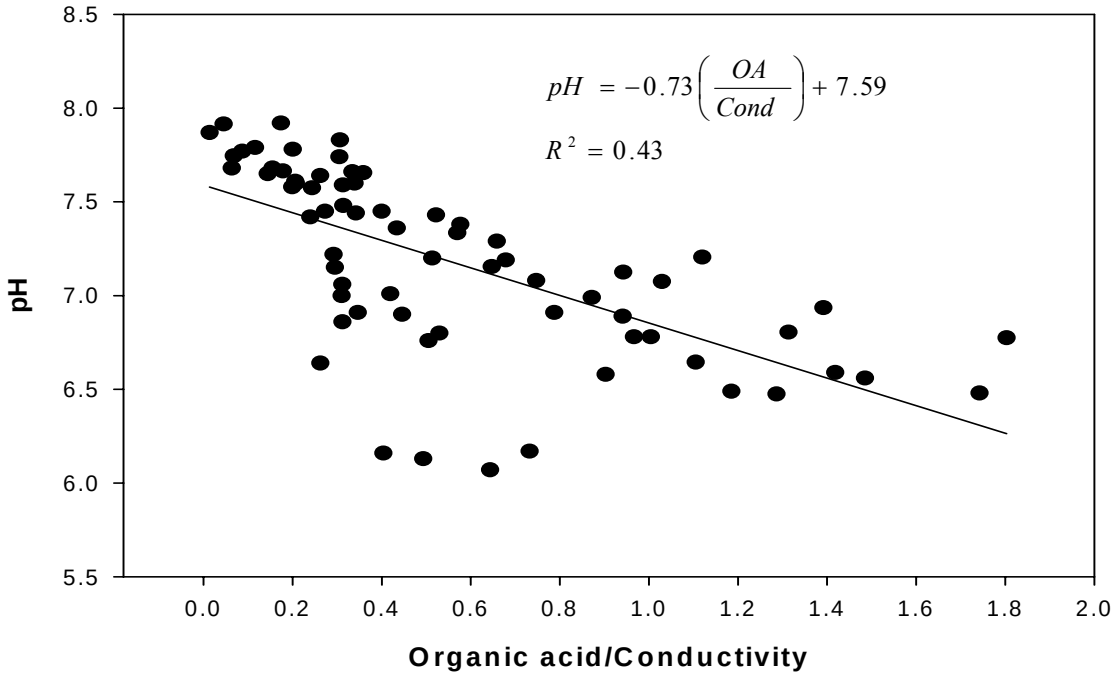


Figure 6.19. pH effect on the organic and conductivity.

From figure 6.19, it was observed that at high OA/Cond ratio, i.e., at low salinity, the pH value was lowered which implies that the alkalinity provided by the salinity is not sufficient enough to buffer the low pH of the hydrolysis. On the other hand, at low OA/Cond ratio, i.e. at high salinity, the alkalinity is sufficiently enough to buffer the system.

It was realized generally that, the total COD produced for each experimental run was higher than the organic acid COD, implying that the leachate contains some other organic solutes, for a example, amino acids, alcohols and sugars.

COD leached per unit mass of dry substance increases with an increase in water to waste ratio as described earlier and also in figure 6.20. The trend is the same as that observed for leaching in figure 6.5 i.e. a decrease of COD/OTS value at low and high ratio of water/waste ratios respectively. It was observed that, for an increase of litre per day of water pumped into the hydrolysis reactor, corresponds to an increase of 4.8 and 47 gCOD per unit mass for the first three experiments, respectively, using the first experiment as a reference point.

But it tends to decrease in magnitude in the order of 18, 54 and 1 gCOD/kgOTS for each litre of water added after the third experiment.

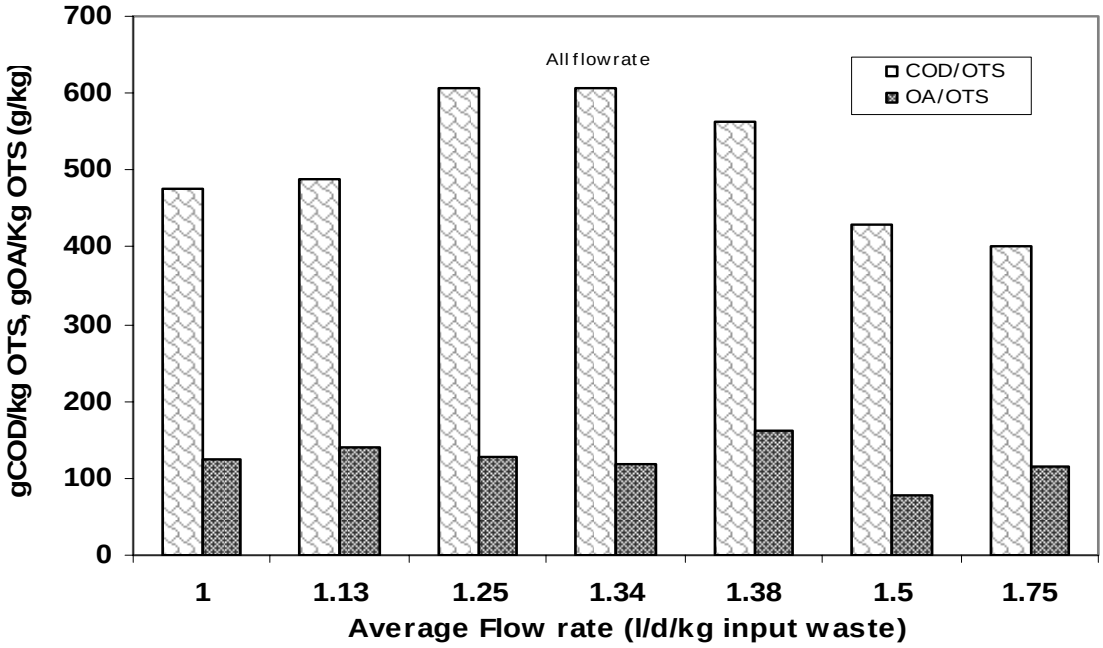


Figure 6.20. The dependence on flow rate to the contribution of COD and organic acid

The variation in OA/OTS with respect to the changing water to waste ratio was not significant and also with no clear cut trend across the experiments. The experiment with variable flow rate regimes showed the second highest COD/OTS ratio. Thus recirculation/flushing the waste bed with the process water intermittently under mesophilic conditions possibly resulted in an optimum hydrolysis performance and eventual shortening of the overall digestion process time.

Variation of COD, OA, BOD, TS ,VOS, conductivity and salinity in the daily leachate concentrations are presented in table 6.2a-6.2g. The data shows the variation in flow rate of water used and the various pollutant concentrations produced.

Table 6.2a-6.2g. Process performance and their pollutant load.

a. Test performance at water flow rate of (1 L/kg input waste.d)

Parameter	Effluent mg/l					% leaching rate				
	Mean	S.D	Median	Min	Max	Mean	S.D	Median	Min	Max
COD	6146	2559	5363	2880	9545	48	1	48	47	48
OA	1669	109	1456	137	3110					
TS	7965	1283	7986	5025	10050					
VOS	3797	707	3709	2596	5191					
Cond	2.22	0.06	2.22	2.15	2.34					
Sal	1.01	0.02	1	1	1.1					
pH	6.13	6.49	7.11	6.01	7.82					
COD:OA	5.83	5.54	3.62	3.06	21.03					
COD:VOS	1.58	0.48	1.65	0.87	2.39					

b. Test performance at water flow rate of (1.13 L/ Kg input waste.d)

Parameter	Effluent mg/l					% leaching rate				
	Mean	S.D	Median	Min	Max	Mean	S.D	Median	Min	Max
COD	6607	251	6034	3240	10255	49	7	49	49	54
OA	1707	921	1873	476	3170					
TS	3983	642	3993	2513	5025					
VOS	4353	2533	3644	1912	997					
Cond	2.29	0.13	2.28	2.09	2.7					
Sal	1.02	0.06	1	0.9	1.1					
pH	7.03	0.48	7.03	6.14	7.76					
COD:OA	4.5	1.53	3.76	3.2	6.80					
COD:VOS	1.76	0.69	1.72	0.69	2.69					

c. Test performance at water flow rate of (1.25 L/kg input waste.d)

Parameter	Effluent mg/l					% leaching rate				
	Mean	S.D	Median	Min	Max	Mean	S.D	Median	Min	Max
COD	6445	5291	4913	1370	17249	61	3	61	59	63
OA	1787	1211	1679	380	3780					
TS	6350	1632	5774	4807	9614					
VOS	2746	1484	2430	1415	5695					
Cond	2.32	0.11	1.10	2.17	2.46					
Sal	1.09	0.09	2.33	1.00	1.20					
pH	6.87	0.82	7.09	4.92	7.68					
COD:OA	3.44	0.72	3.38	2.59	4.59					
COD:VOS	2.03	0.80	1.99	0.97	3.03					

d. Test performance at water flow rate of (1.38 L/kg input waste.d)

Parameter	Effluent mg/l					% leaching rate				
	Mean	S.D	Median	Min	Max	Mean	S.D	Median	Min	Max
COD	5281	3270	4603	1828	12295	56	5	56	53	60
OA	1239	1266	771	110	3957					
TS	10252	2841	10670	5298	14486					
VOS	3734	1377	2850	2405	5703					
Cond	2.34	0.09	2.36	2.15	2.46					
Sal	1.08	0.04	1.1	1	1.1					
pH	7.4	0.43	7.55	6.45	8.01					
COD:OA	7.56	4.78	6.20	3.10	16.55					
COD:VOS	1.35	0.49	1.2	0.76	2.16					

e. Test performance at water flow rate of (1.5 L/kg input waste.d)

Parameter	Effluent mg/l					% leaching rate				
	Mean	S.D	Median	Min	Max	Mean	S.D	Median	Min	Max
COD	4131	3485	2476	1200	12060	43	3	43	41	45
OA	789	707	514	30	2299					
TS	5151	1200	4742	3956	7912					
VOS	1990	985	1927	316	3906					
Cond	2.54	1.13	2.19	2.07	5.77					
Sal	1.19	0.64	1	0.9	3					
pH	7.34	0.58	7.55	6.13	7.9					
COD:OA	8.87	11.13	5.27	3.96	40.44					
COD:VOS	2.07	0.99	1.66	0.93	3.79					

f. Test performance at water flow rate of (1.75 L/ Kg input waste.d)

Parameter	Effluent mg/l					% leaching rate				
	Mean	S.D	Median	Min	Max	Mean	S.D	Median	Min	Max
COD	3125	1409	2987	1308	6208	40	3	40	38	42
OA	889	230	760	681	1381					
TS	4549	865	4614	2649	5356					
VOS	1414	314	1385	1056	2112					
Cond	2.48	0.12	2.49	2.28	2.28					
Sal	1.14	0.07	1.15	1	1.2					
pH	6.93	0.18	6.91	6.64	7.22					
COD:OA	3.42	0.9	3.59	1.72	4.49					
COD:VOS	2.14	0.59	2.08	1.2	2.94					

g. Test performance at stepwise decrease from (1 – 1.75 L/kg input waste .d)

Parameter	Effluent mg/l					% leaching rate				
	Mean	S.D	Median	Min	Max	Mean	S.D	Median	Min	Max
COD	5762	4081	4868	2235	15215	61	2	61	59	62
OA	1188	665	795	679	2574					
TS	5318	1011	4964	3709	7418					
VOS	2331	683	2009	1802	3893					
Cond	2.59	0.48	2.42	2.21	2.36					
Sal	1.76	0.86	1.1	1.1	3.1					
pH	7.34	0.50	7.54	6.16	7.83					
COD:OA	4.66	0.87	4.44	3.27	5.91					
COD:VOS	2.29	0.97	1.78	1.58	3.91					

Anaerobic activities in the hydrolytic reactor. The gas phase study of the hydrolytic reactor was carried out by measuring the daily gas composition as presented in figure 6.21.

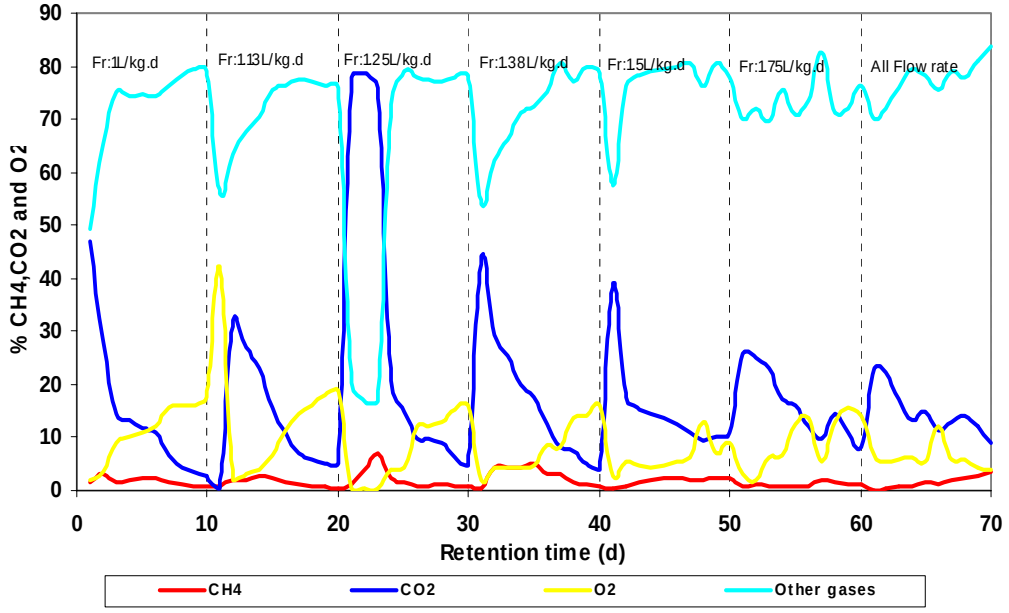


Figure 6.21. Gas production during hydrolysis as a function of operational time of each test.

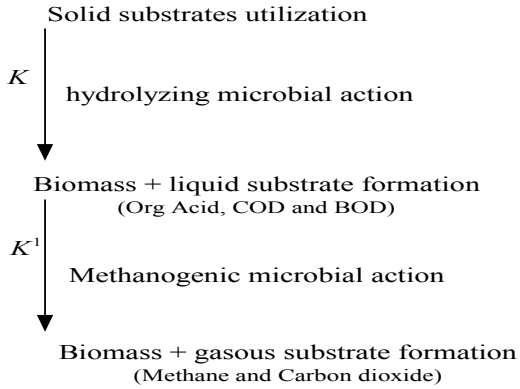
Methane production in the hydrolytic reactor was generally not significant with an average value of 1.8±1.3% ranging from a minimum of 1% to a maximum of 7.2%. This behaviour of gas production was expected, due to the low methanogenic biomass concentration in the hydrolytic reactor as a result of the low pH and the effect of micro oxygen (average oxygen composition 8.3±5.1%) in the reactor. The methanogens are sensitive to oxygen, therefore the micro-oxygen application based on the reactor design was aimed at suppressing any appreciable methanogenic activity during hydrolysis. Generally, as shown in figure 6.21, during hydrolysis the methane concentration shows a decrease when the oxygen concentration increases. It can be deduced that, the suppression of the methanogenic activity in the hydrolytic reactor to a greater extent was due to the presence of oxygen. Because, within the first 6 days where oxygen concentration was low, the methane production appears to increase, but started to decrease as the oxygen concentration

increases. Hence, the microaerophilic technique to a large extent was successful in preventing an appreciable methane production in the hydrolytic reactor. This implies that methanogenic activity was effectively inhibited. The CO_2 concentration was quite high (18±16%) having a minimum of 2.8% and a maximum of 79%. This scenario was expected since during acidogenesis CO_2 is one of the main components produced along side with organic acid and hydrogen. For the other gases produced apart from CH_4, CO_2 and O_2, much could not be commented since further test was not conducted to analyse their composition and also it was of no interest with respect to the focus of the research. In summary, no significant biogas production was registered in the hydrolysis reactor. Pavan et al. (2000) reported a similar result from anaerobic hydrolysis of fruit and vegetable waste.

Kinetic model for substrate utilization . As already explained in section 4.5.4, the first-order kinetic model is more appropriate for complex wastes such as the one being used in this experiment for which hydrolysis plays an important role (Pavan et al., 2000). It has also been reported that solid hydrolysis is the rate limiting step in anaerobic digestion of cellulose (Kübler et al., 1994).

In the anaerobic digestion, solid forms of biomass are converted into liquid forms by using hydrolyzing microorganisms. As a result liquid are enriched with carbon compounds which is designated as COD. These carbons are then converted into gaseous form such as methane and carbon dioxide by using microorganisms. Some amount of it is used for cell growth and maintenance. So solid carbon particles are converted into gaseous carbon through liquid carbon which is the main substrates for the methanogenesis.

According to figure 4.11, the following major reaction steps are involved in the anaerobic digestion of particulate matter to methane.



Assuming the first order degradation pattern was followed by hydrolytic process, then, the rate of degradation of particulate organic matter can be written as

$$-dc/dt = KC$$

With :

$$-dc/C = Kdt$$

It follows :

$$\ln C/C_o = Kt$$

$$\Rightarrow$$

$$C = C_o * \exp^{(-kt)} \qquad 4.21$$

Where, C = *Substrate concentration at time t in g / litre*,
C_o = *Initial substrate concentration in g / litre and*
K = *Rate cons* tan *t in days*.

Further int *egration wrt t leads to*

$$\frac{dC}{dt} = \left[C_o \cdot \exp^{(-k_H \cdot t)}\right]dt \qquad 4.22$$

Finally gives

$$C = C_o\left(1 - \exp\left(-k_H \cdot t\right)\right) \qquad 4.23$$

Using equation 4.23 the statistical analysis delivered values for correlation coefficient, hydrolysis rate constant K_H and standard deviation of error based on the change of COD values between experimental and predicted valuables are presented in table 6.3. These were obtained by solving the non-linear first–order equation by exponential regression analysis and the main parameters shown in Table 6.3.

Table 6.3. Statistical analysis of COD values

Flow rate (L/kg.d)	Correlation coefficient	K_H– Values day^{-1}	Standard deviation of error
1.00	0.98	0.052	0.022
1.13	0.99	0.0830	0.018
1.25	0.98	0.241	0.028
1.38	0.99	0.141	0.019
1.50	0.99	0.128	0.013
1.75	0.99	0.112	0.015
Stepwise decrease (all flow rate)	0.98	0.268	0.029

Table 6.4. Hydraulic retention time, determined first-order hydrolysis rate constant and starting concentration of biodegradable particulate polymers.

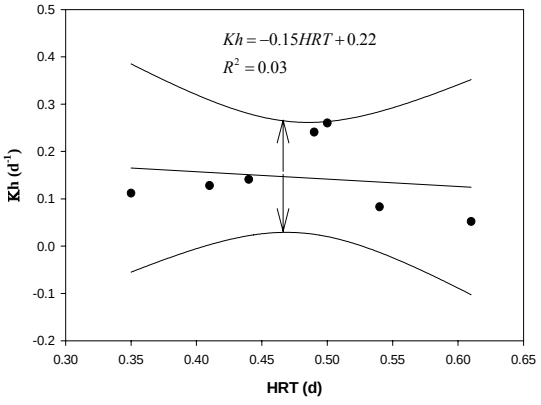
HRT (d)	K_H (d-1)	Starting COD concentration(g/l)
0.61	0.052	3190
0.54	0.083	2680
0.49	0.241	1800
0.44	0.141	2030
0.41	0120	1627
0.35	0.112	1630
All HRTs	0.268	1630

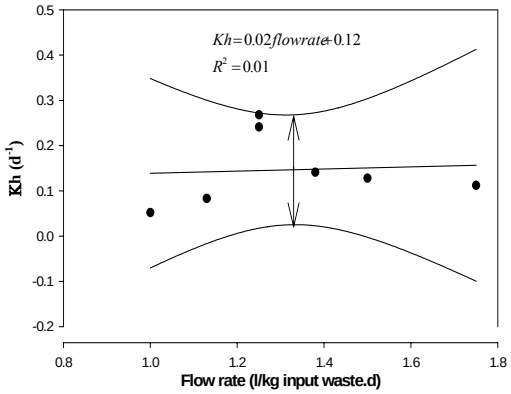
The values of the kinetic constants obtained in this research are comparable with values of other studies on double stage fermentation of OFMSW.

Table 6.5. Experimental conditions and hydrolysis rate constants determined.

K_H (d-1)	Temp oC	Literature	Type of waste
0.052-0.268	30±2	Current study	Biowaste (food remains, fruit and vegetables)
0.060-0.240	30	Veeken et al 2000	Biowaste (branches, leaves, roots an lumps of grass and barks
0.076-0.264	30	Veekeen and Hamelers 1999	Biowaste (bread, oranges, leaves and barks)

From 99% confidence interval, the obtained hydrolysis constant was regressed with the HRT and the flow rate regime as shown in figure 6.22.





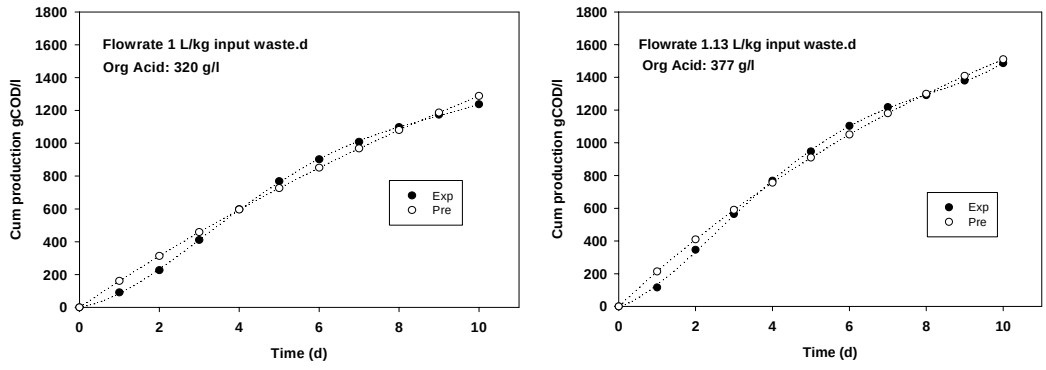
$$Confidence\ \ region\ ,\ \varepsilon = \hat{y} \pm t_{\alpha}.s_{\hat{y}}$$
$$\alpha = significan\ t\ level\ = 0.01$$
$$\varepsilon = 1 - \alpha\ confidence\ \ level\ = 99\%$$
$$s_{\hat{y}} = s\tan dard\ \ deviation\ = \sqrt{s_{\hat{y}}{}^{2}}.\frac{(x-\bar{x})^2}{n\sum(x)^2}$$

Figure 6.22. Hydrolysis rate constant as a function of HRT and flow rate regime within a confidence interval.

Statistical analysis of the average hydrolysis rate constants in different monitoring phases for the seven sets of experiments obtained by means of hypothesis testing, shows that the values were within 99% confidence interval valid.

Figure 6.23 shows the total production of soluble COD at various flow rate regimes calculated by using a simple mass balance equations around the hydrolysis reactor and the function in equation 4.23 for the different dilution conditions.

The curves of production of total soluble COD and fermentation products show a typical first-order rate pattern, namely, a high rate at the start, which then levels down in time. For experiments at water flow rate of 1.3 l/kg.d, 1.25 l/kg.d, stepwise decrease, 1.38 l/kg.d and 1.5 l/kg.d had corresponding cumulative COD values of 1486.49, 1503.46, 1371.36, and 1564 gCOD/l respectively, which were the highest and almost equal. The organic acid productions were also 376.97, 336.75, 382.56 and 397.57g/l respectively. This indicates 22 to 28% acidification which means that there was more accumulation of monomeric products. In other words, it indicates that hydrolysis of particulate matter proceeds faster and the fermentation of monomers is the rate limiting step. However, for runs at flow rate at 1 and 1.75 l/kg.d, a cumulative COD values were 1237 gCOD/l and 1068 gCOD/l respectively. The corresponding cumulative organic acid production were 320 g/l and 327 g/l respectively. Though, the cumulative COD production were lower, the fermentation products measured as organic acid were equally the same as all the process.



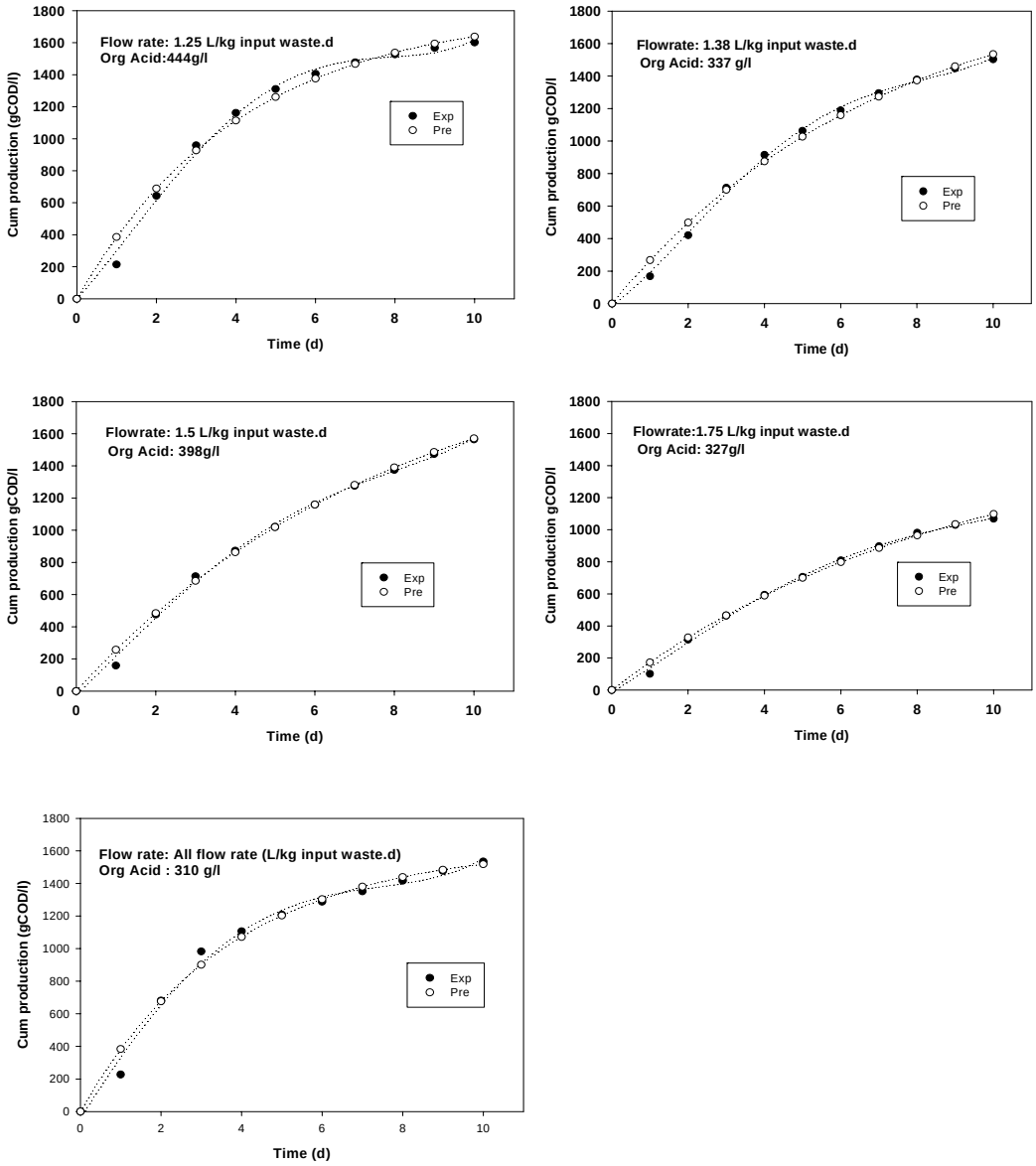


Figure 6.23. Cumulative production of total soluble COD and organic acid concentrations

The experimental values of the cumulative COD produced were compared with the predicted values (figure 6.24).

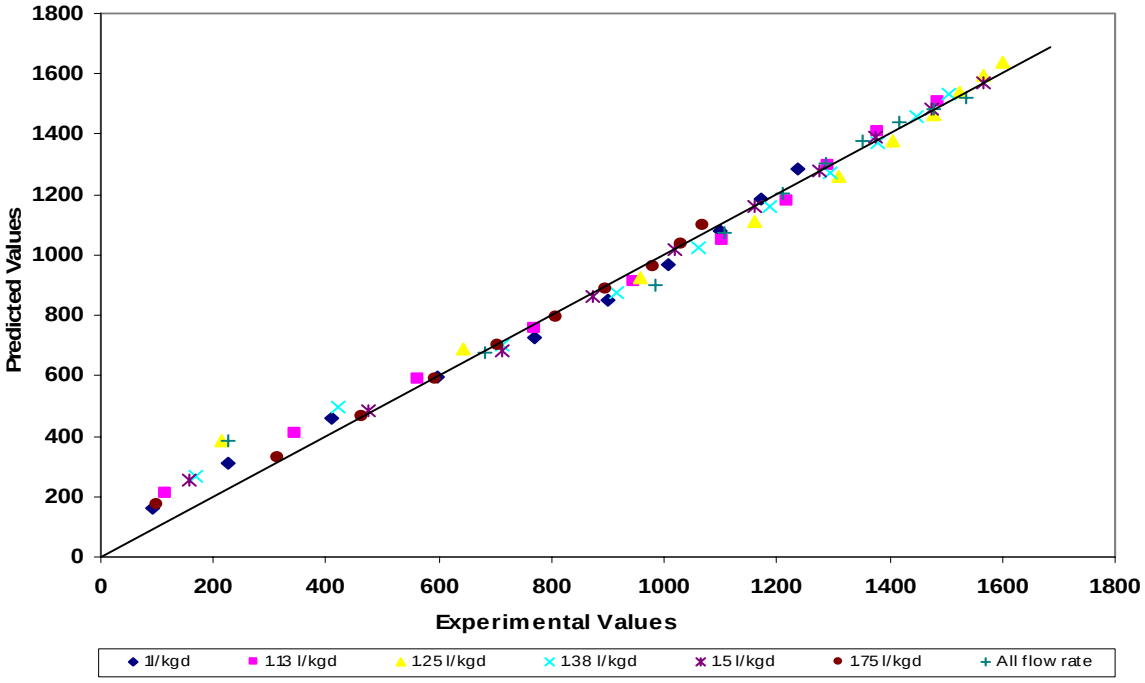


Figure 6.24. Time courses of experimental and predicted values of COD

The deviation between experimental and predicted values is not greater than 18%. The small deviations obtained (lower than 18%) in all the cases suggest that the proposed first-order model and COD balance predict the behaviour of the reactor for the treatment of UMSW very accurately and that the parameters obtained represent the activity of the microorganisms affecting the anaerobic digestion of this waste at mesophilic temperature.

6.3.3 The second stage of the set-up

Buffer tank. After the leached liquid leaves the hydrolytic reactor, it goes directly into the storage tank described previously as the buffer tank where it is maintained at a temperature less than 13^{o}C. The presence of the buffer was necessary considering the nature of the waste. A lot of sedimented material (sand, seeds, pieces of leaves and plastics) were observed which often block the tubes delivering liquid to the methane reactor. A variation was observed between the hydrolytic COD measured and that stored in the buffer tank which implies further degradation could have taken place whiles in transition despite the storage temperature. It could merely be as a result of dilution. A summary of the characteristics of the liquid in the buffer are presented in table 6.6a-6.6h. An overall average variation of 27±14% increment was observed for the buffer

tank COD with corresponding 34±32% increment for the organic acid. This variation of hydrolysis and buffer COD, also gives rise to a variation between the ratio of the minimum and the maximum values in both systems – an average of 14±13 in the hydrolysis reactor to 6±3 in the buffer reactor.

It was also observed that the mean pH values of the buffer was 10% higher than in the hydrolysis. The lowest pH observed in the buffer was 5.32 and the corresponding value in the hydrolysis was 4.92, which imply 8% higher. Similarly, 4% higher was observed between the highest pH measured in the hydrolysis and the buffer (7.83 to 8.17). The general increase of pH from the hydrolysis to the buffer tank – could be due to dilution.

Table 6.6a-6.6h. Summary of the most relevant parameters for the various flow rate regimes.

a. Test performance at HRT of 5.5 days flow rate regimes

Parameter	Influent mg/l					Effluent mg/l					% removal rate		
	Mean	S.D	Median	Min	Max	Mean	S.D	Median	Min	Max	Mean	S.D	Median
COD	6762	2757	7441	3195	10450	820	151	854	405	930	86	7	89
BOD_5	3980	56	3980	3940	4020	75	7	75	70	80	98	0.2	98
OA	1820	994	1707	474	3242	21	3	21	15	26	98	0.9	99
Cond	1.65	0.16	1.72	1.43	1.85	1.9	0.13	0.7	1.7	2.04			
Sal	0.64	0.1	0.72	0.5	0.8	0.86	0.07	0.9	0.7	0.9			
pH	7.43	0.52	7.63	6.4	8	7.8	0.13	7.63	7.97	7.97			
COD:BOD	2.04	0.03	2.04	2.01	2.06	10.97	1.03	10.3	10.23	11.70			
COD:OA	4.27	1.56	4.39	2.34	6.73	40	10	39	18	56			
COD:VOS	1.7	0.58	1.48	1.11	2.78								

b. Test performance at HRT of 4.9 days flow rate regimes

Parameter	Influent mg/l					Effluent mg/l					% removal rate		
	Mean	S.D	Median	Min	Max	Mean	S.D	Median	Min	Max	Mean	S.D	Median
COD	7891	2643	7763	3250	10350	703	153	756	322	825	88	6.2	92
BOD_5	4230	99	4230	4160	4300	98	18	98	85	110	98	0.5	98
OA	1887	1046	1902	343	3134	37	13	36	18	57	97	1.2	98
Cond	1.51	0.16	1.57	1.22	1.68	2.01	0.12	2.05	1.69	2.11			
Sal	0.9	0.22	0.6	0	0.9	0.9	0.1	0.9	0.7	1.1			
pH	7.26	0.50	7.32	6.34	7.87	7.69	0.15	7.67	7.49	7.91			
COD:BOD	1.44	0.33	1.44	1.41	1.47	7.6	1.37	7.6	6.62	8.57			
COD:OA	4.65	2.14	3.77	2.85	9.49	22	12	19	8	43			
COD:VOS	2.4	0.41	2.25	1.89	2.97								

c. Test performance at HRT of 4.4 days flow rate regimes of influent

Parameter	Influent mg/l					Effluent mg/l					% removal rate		
	Mean	S.D	Median	Min	Max	Mean	S.D	Median	Min	Max	Mean	S.D	Median
COD	8300	3788	7813	3400	13650	349	57	366	187	380	94	3	96
BOD_5	6118	247	6135	5800	6400	76	15	80	55	90	98	0.3	99
OA	2194	1074	2300	610	3410	48	5	49	40	55	97	2	98
Cond	1.97	0.10	1.97	1.82	2.1	2.33	0.07	2.35	2.33	2.44			
Sal	0.8	0.07	0.8	0.7	0.9	1.06	0.05	1.1	1	1.1			
pH	7.02	0.88	7.22	5.32	7.99	7.98	0.06	8	7.89	8.05			
COD:BOD	1.33	0.05	1.33	1.27	1.4	4.68	1.1	4.32	3.83	6.25			
COD:OA	3.97	0.68	3.82	3.29	5.57	7.34	1.41	7.32	4.36	9.25			
COD:VOS	2.11	0.42	2.03	1.43	2.7								

d. Test performance at HRT of 4.0 days flow rate regimes of influent

Parameter	Influent mg/l					Effluent mg/l					% removal rate		
	Mean	S.D	Median	Min	Max	Mean	S.D	Median	Min	Max	Mean	S.D	Median
COD	6828	2702	7241	3456	10155	878	163	930	428	990	85	7	88
BOD_5	2540	255	2540	2360	2720	173	95	173	105	240	93	3	93
OA	581	596	405	23	1794	23	21	19	1	59	95	0.8	95
Cond	1.93	0.2	1.96	1.54	2.22	2.38	0.11	2.43	2.19	2.5			
Sal	0.8	0.12	0.8	0.6	1	1.09	0.06	1.1	1	1.2			
pH	7.8	0.5	7.9	7.0	8.4	7.5	0.01	7.5	7.5	7.6			
COD:BOD	2.6	0.26	2.6	2.43	2.8	6.18	3.42	6.18	3.77	8.60			
COD:OA	4.6	49	27	3.94	147	205	298	56.5	9.5	908			
COD:VOS	2.78	1.24	3.17	0.96	4.3								

e. Test performance at HRT of 3.7 days flow rate regimes of influent

Parameter	Influent mg/l					Effluent mg/l					% removal rate		
	Mean	S.D	Median	Min	Max	Mean	S.D	Median	Min	Max	Mean	S.D	Median
COD	5863	2784	5008	1390	10130	360	60	376	190	390	93	4	93
BOD_5	3477	326	3660	3100	3670	270	69	310	190	310	92	3	92
OA	1462	945	1225	340	2790	54	30	47	10.3	95	96	2	96
Cond	2.10	0.71	1.90	1.59	4.1	2.93	1.57	2.21	1.98	6.42			
Sal	0.96	0.69	0.75	0.6	2.90	1.41	1.0	0.95	0.8	3.5			
pH	7.44	0.72	7.52	6.23	8.25	8.09	0.27	8.05	7.8	8.57			
COD:BOD	2.04	0.71	1.75	1.59	3.08	1.56	0.43	1.56	1.19	1.93			
COD:OA	4.58	1.4	3.9	3..3	7.32	10.65	10.5	6.66	3.82	37.75			
COD:VOS	1.69	0.36	1.84	0.77	1.89								

f. Test performance at HRT of 3.1 days flow rate regimes of influent

Parameter	Influent mg/l					Effluent mg/l					% removal rate		
	Mean	S.D	Median	Min	Max	Mean	S.D	Median	Min	Max	Mean	S.D	Median
COD	3538	1435	3272	2020	6040	301	96	320	150	450	91	2.2	92
BOD_5	1558	143	1505	1450	1720	21	12	15	13	35	93	0.3	94
OA	1004	249	935	714	1418	60	32	62	16	101	94	2.8	93
Cond	1.70	0.27	1.68	1.41	2.08	2.33	0.22	2.30	2.11	2.81			
Sal	0.70	0.14	0.8	0.50	0.8	1.01	0.07	1.0	0.9	1.1			
pH	7.38	0.18	7.38	7.2	7.71	7.71	0.08	7.68	7.57	7.85			
COD:BOD	2.32	0.20	2.39	2.08	2.47	17.75	7.95	20.41	8.80	24.0			
COD:OA	3.46	0.87	3.25	2.48	4.62	5.90	2.01	4.85	3.81	9.22			
COD:VOS	1.59	0.57	1.47	1.03	2.57								

g. Test performance at stepwise decrease of all HRTs flow rate (3.6 days) regimes of influent

Parameter	Influent mg/l					Effluent mg/l					% removal rate		
	Mean	S.D	Median	Min	Max	Mean	S.D	Median	Min	Max	Mean	S.D	Median
COD	8535	3802	7373	4300	15370	342	61	358	173	380	95	2.0	95
BOD_5	5317	499	5235	4800	6000	30	14	25	20	50	99	0.2	99
OA	1938	496	1995	1220	2510	26	11	26	11	39	99	0.3	99
Cond	2.29	0.66	2.07	1.92	4.13	3.05	1.21	2.36	2.21	4.86			
Sal	1.05	0.65	0.90	0.70	2.80	1.50	0.79	1.05	1.00	2.70			
pH	7.64	0.46	7.70	6.60	8.17	8.32	0.13	8.35	8.07	8.48			
COD:BOD	1.57	0.14	1.59	1.38	1.73	12.97	4.9	14.10	6.79	16.91			
COD:OA	4.32	1.27	3.72	3.14	6.33	15.46	7.08	13.54	9.25	31.65			
COD:VOS	2.49	0.52	2.47	1.84	3.13								

h. Experimental results for the overall performance at all flow rate regimes of influent

Parameter	Influent mg/l					Effluent mg/l					% removal rate		
	Mean	S.D	Median	Min	Max	Mean	S.D	Median	Min	Max	Mean	S.D	Median
COD	6694	3213	6455	1390	15370	536	260	380	150	990	90	6.39	92
BOD_5	4012	1638	4020	1450	6400	104	92	80	12.89	310	97	2.3	98
OA	1555	956	1385	23	3410	38	24	36	1.09	101	97	2.14	97
NH_4-N	220	106	210	100	380	382	119	400	130	610			
pH	7.42	0.60	7.48	5.32	8.37	7.88	0.28	7.85	7.49	8.57			
COD:BOD	1.85	0.52	1.60	1.27	3.08	8.64	6.34	6.79	1.60	24.05			
COD:OA	10.03	22.70	4.05	2.34	147	56	146	13.20	3.81	908			
COD:VOS	2.11	0.76	1.96	0.77	4.34								

The most essential activities taking place in the methane stage is presented in the section below.

The methanogenic stage. *BOD and COD removal.* The maximum values recorded for the COD and BOD influents demonstrate the ability of the system to deal with occasionally high organic loads. Similarly, the minimum values of the effluent liquid exiting the methane reactor demonstrates the potential for very good performance. The organic loading removal rate was 0.2-0.9 kg/m^3 reactor day for BOD and 0.7-2.5 kg/m^3 reactor day for COD based on an average daily hydraulic loading of 0.8-4.8 kg/m^3 reactor day, calculated from pump data.

The reduction of COD, BOD and OA were similar, 90±6, 97±2.3 and 97±2.1 % respectively (table 7.6h). Kübler et al 1994 reported 79% removal of dissolved COD plus eliminated solids COD were converted to methane at a loading rate of 19 kg COD m^{-3}d^{-1}. In this regard the action of the double stage digester is unique compared to other biological systems. The influent ratio of COD and BOD showed a median of 1.6, the ratio after treatment was 6.8 (table 6.6h). The increased rate of BOD removal indicates the extent of biodegradable in the influent which is biodegradable and this is in line with conventional biological treatment systems, where BOD removal rates exceed COD removal rates.

Figure 6.25 shows the overall COD removal efficiency and organic loading rate as a function of operational time at various HRTs.

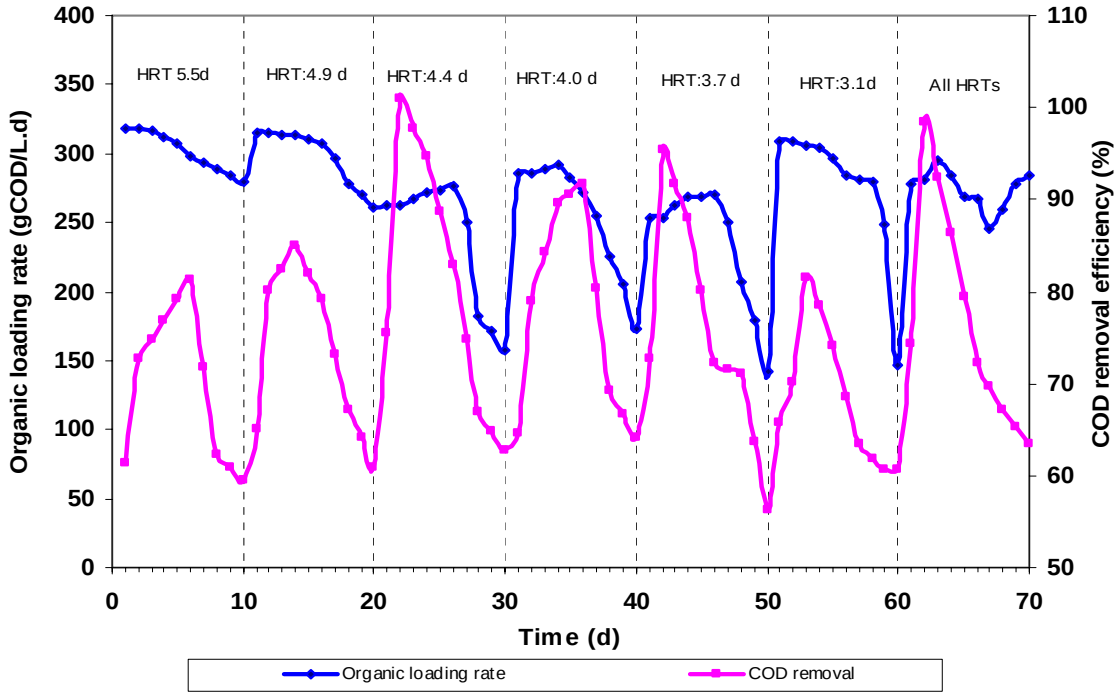


Figure 6.25. Temporal variation of COD removal efficiency and organic loading rate as function of operation time at different HRTs.

For each experimental phase, it was observed that COD removal efficiency increases at higher influent concentration and decreases at lower influent concentrations, especially getting to the end of that experimental period.

Yeh et al. (1997) observed similar trend of COD removal when treating wastewater using anaerobic rotating biological contactor.

Therefore, high COD removal efficiencies were observed when the reactor was subjected to high COD concentrations. COD removal efficiencies of 94% and 95% were achieved after very stable operation for high average influent COD concentrations of 8535 and 8300 mg/l for HRTs of 4.4 and 'all HRTs' (HRT of 3.6 d) respectively. Similarly, the same efficiency was observed for both BOD and OA removal according to table 6.6c and 6.6g. This was an indication that COD was really removed from the liquid but not converted into any intermediary products. This is because the organic acid production rate can be directly related to COD removal rate (Yeh et al., 1997).

In summary, equally high COD removal trend of 88% to 93% was observed for the entire operating conditions (table 6.6a-6.6g). High COD removal efficiencies were observed when the reactor was subjected to higher COD concentrations. This trend satisfies the hypothesis that higher feeding rate leads to increase in feeding rate of the microorganisms leading to a higher production of bacterial biomass. It has been reported that the microbe breeding rate increases with increasing influent COD content. The effluent pH ranged from 7.5 to 8.6 for the entire experimental conditions imposed. The effluent salinity was always higher than those observed in the influent stream, thus indicating leaching of ions into solution. It also confirms leaching of metals as suggested in literature as one of the advantages of a double-stage reactor.

High average degradation results of 96% for OA in the methane reactor at pH between 7 and 8 was achieved. The pH never gave rise to particular problems of instability and remained in the typical range for mesophilic anaerobic digestion. It allowed me to conclude that there is no need to control the pH in the methane reactor at any of the loading rate. The effect of HRT on COD removal was pronounced at lower and higher values of HRT. Lower removal efficiencies occurs at both extremely low and high HRTs. It was observed that removal efficiencies of COD and BOD does not show a significant pattern of decrease when HRT was decreased. This pattern was evident at a high volume liquid feeding (low HRTs of 3.7d) in figure 6.25.

It was realized that, generally removal efficiencies increases with an increase in the influent strength, i.e., there was a linear correlation between COD removal and COD strength which indicates that the influent strength was not a limiting factor in these tests.

Therefore, since COD and BOD removal do not decrease at high organic loading rates, it would be practical to load the system at a higher organic loadings. Hence, it can be deduced that the

slurry bed system of the double stage is an effective treatment process at HRT less than 4 and influent COD concentrations between 1390 and 15370 mg/l. Nevertheless an optimization routine must be performed in order to evaluate the exact HRT to be applied for each influent of COD concentration condition. Such routine can result in the establishment of the process limits, thus resulting in more compact units, besides providing information on toxicity and inhibition levels.

(COD:BOD) ratio. The COD value for the leachate will always be higher than the BOD. It varies from a ratio of 1.25 to 2.50 for influent domestic wastewaters. In conventional biological treatment systems the ratio increases with each stage of biological treatment with ratios > 10:1 expected in the final effluent. The ratio between COD and BOD increases across the methane reactor system which is in line with literature.

Biogas production. The average daily biogas and methane production profile is presented in figure 6.26. Generally, the trend of daily biogas production presented in figure 6.26 follows a similar trend like COD production during hydrolysis. Having the highest daily gas production within the first 2 days and then levels down to a minimum value. An average of 66±46 l/d of biogas with average methane quality of 71±5 % and carbon dioxide concentration of 18±34% were recorded.

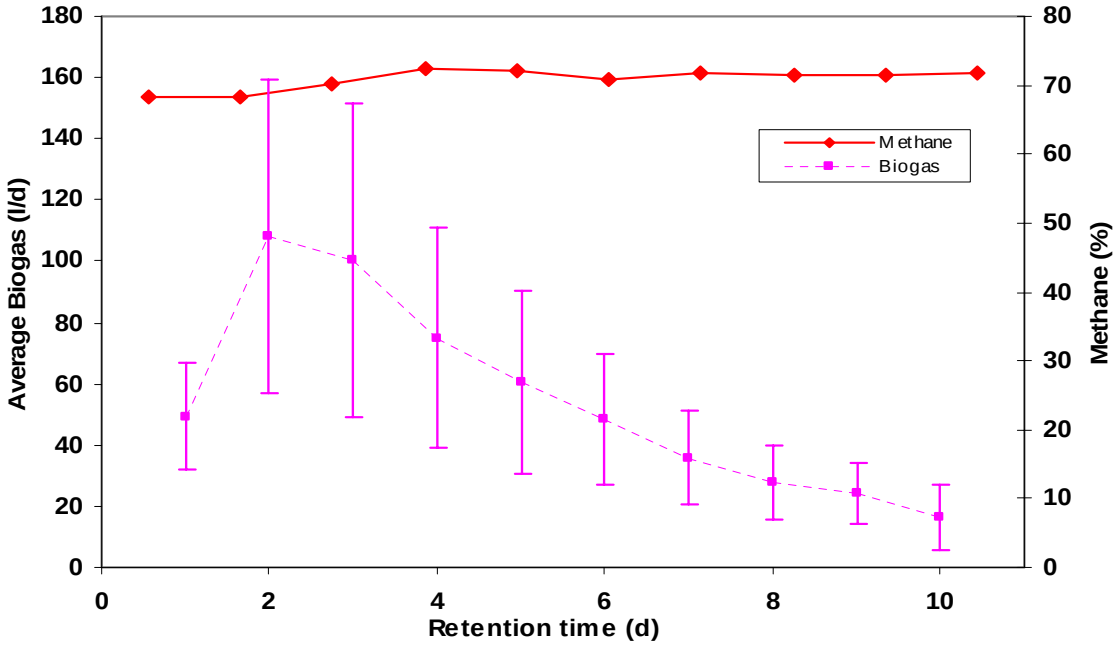


Figure 6.26. Daily average biogas production and the its methane concentration.

Oxygen and other trace gases which were not identified are also presented in figure 6.27.

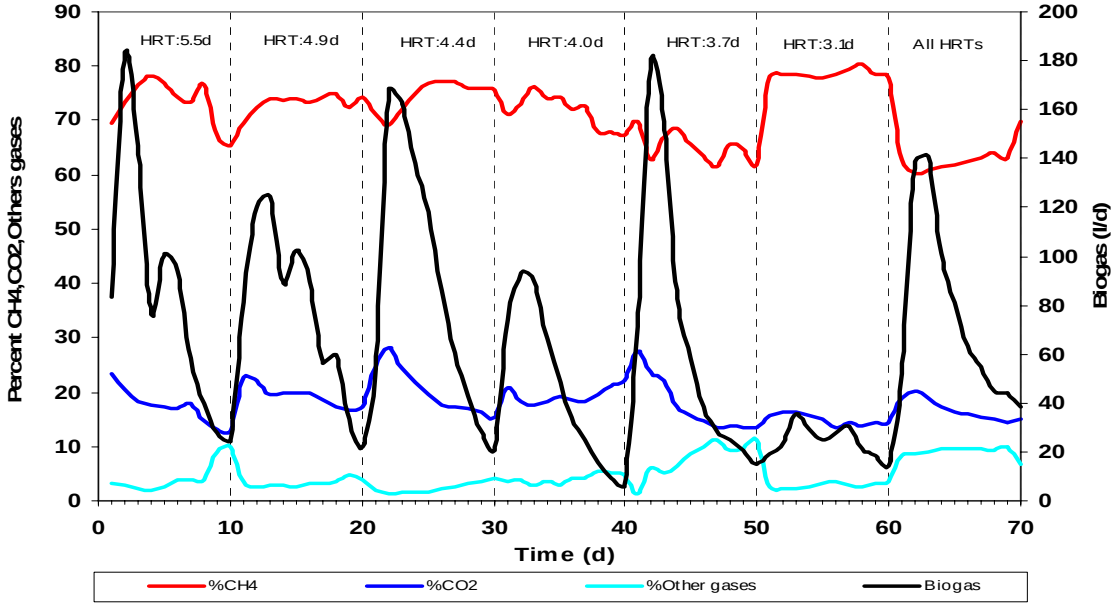


Figure 6.27. Individual gas composition observed for all test. The broken lines separates each experimental run from the other.

It was observed that methane composition shows a slight decrease at the beginning of each of the experiments where concentrations are optimum.

The influence of HRT on biogas production. The gas production profile for each separate test conducted with different HRTs in the methane reactor is presented in figure 6.28.

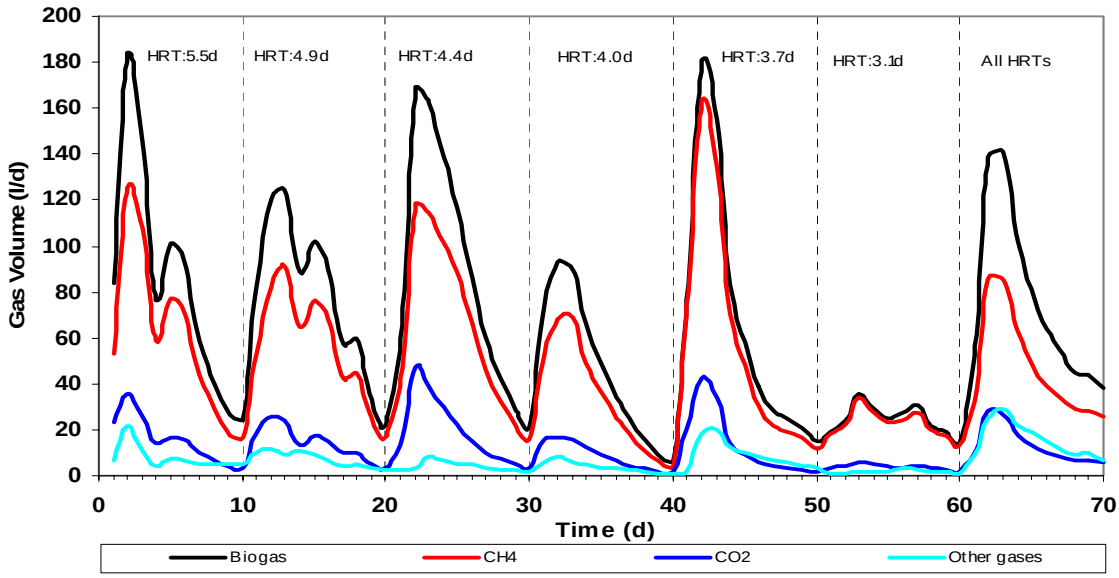


Figure 6.28. Average daily gas production registered during the course of each experiment at variable HRT. The broken lines separates each experimental run from the other.

The effect of very low HRT (high flow rate of 35l/d) was significant. The trend obtained for the remaining test indicates no clear cut variation between biogas production and HRT. A probable influence on gas production behaviour could be attributable to the characteristics of the waste (i.e. the quality of the input waste).

In the experiments, where flow rate was increased to 35 l/d of process water with corresponding lower HRT (0.35 d) in the hydrolytic reactor, leached products such as COD and organic acid were lower (table 6.2f). The effect of lower COD leached was also reflected in the gas production yield for that experiment as can be seen in figure 6.28. The test with HRT at 4.0 days (liquid flow rate of 27.5 l/d) also showed a lower yields. A significantly lower concentration of 581 mg/l organic acid was observed (table 6.6d), lower than all the organic acid concentrations of the tested HRTs. Less organic acid load coming from the buffer tank could induce significant lower yields in the methanogenic phase. The lower OA acid concentration in the first stage may be attributed to the fact that most of the organic compounds could have been biodegraded and converted to OAs in the first stage, but significant fraction were further converted to methane in that same first stage. In support of this assumption made, figure 6.21 is revisited. The gas composition monitored in the hydrolytic phase indicated slightly higher methanogenic activity for HRT at 4.0 days compared to the rest of the experiments. This implies that part of the COD could have been lost to methane production. Another possible explanation could come from the characteristics of the waste fed to the hydrolysis reactor in the first phase which could be poor in terms of producing quality COD and this could probably be the reason even though, the overall COD production was substantial.

A summary of the daily average daily loading rates and its corresponding biogas and methane production is presented in table 6.7 and 6.8 respectively.

Table 6.7. Summary of the average daily loading rate and the specific biogas yield.

Test	Org.Load (gCOD/l_r .d)					Specific Gas Prodtn (l/kgCOD.d)				
HRT(d)	Mean	SD	Median	Min	Max	Mean	SD	Median	Min	Max
5.5	1.2	0.5	1.4	0.6	1.9	323	153	252	192	600
4.9	1.5	0.5	1.6	73	2.1	250	73	248	150	405
4.4	1.9	0.9	1.8	85	3.1	391	90	386	245	510
4.0	1.7	0.7	1.8	95	2.5	241	204	186	46	682
3.6*	1.6	0.7	1.4	90	2.9	417	43	420	322	499
3.7	1.6	0.8	1.4	42	2.7	346	147	308	179	594
3.1	1.1	0.5	1.0	70	1.9	214	61	195	153	338

L_r=L of digester

An overall average of 1.5±0.28 gCOD/$l_{reactor}$.d was delivered to the methane reactor with a minimum of 1.1 gCOD/ $l_{reactor}$.d to a maximum of 1.9 gCOD/ $l_{reactor}$.d. Christ et al, (1999) reported that, a COD volume load of 1 to 4 gCOD/ $l_{reactor}$.d corresponds to an organic volume

load of approximately 0.8 to 3 gVSS/ $l_{reactor}$.d which is within range for which municipal sewage-sludge digesters are suitable

Consequently, an overall average of 311±78 l/kgCOD of biogas was obtained with a minimum of 214 l/kgCOD at HRT of 3.1 days and a maximum of 417 l/kg COD at HRT of 3.6 days.

However, the methane production attained an average of 216±49 l/gCOD with a range from a minimum of 166 to 290 l/kgCOD.

The total biogas production rate increased as the HRT decreased or the influent COD increased. That is, the biogas production was enhanced at higher organic loading rates. This is due to the fact that more organic matter is biodegraded and converted to biogas at higher organic loading rates.

Table 6.8. Summary of the average daily loading rate and the specific methane yield.

Test	Org.Load (gCOD/l_r .d)					Specific Methane Prodtn (l/kgCOD. d)				
HRT(d)	Mean	SD	Median	Min	Max	Mean	SD	Median	Min	Max
5.5	1.2	0.5	1.4	0.6	209	229	101	186	128	413
4.9	1.5	0.5	1.6	73	232	175	46	176	111	262
4.4	1.9	0.9	1.8	85	339	290	62	297	185	360
4.0	1.7	0.7	1.8	95	278	166	138	131	31	479
3.6*	1.6	0.7	1.4	90	323	228	100	208	114	394
3.7	1.6	0.8	1.4	42	302	166	47	153	120	260
3.1	1.1	0.5	1.0	70	211	260	26	260	203	302

L_r=L of digester

Finding whether the specific gas production changes at higher organic loads. Considering experiments with HRTs of 5.5, 4.4, 3.7 and 3.1, which corresponds to influent flow rate regimes of 20, 25, 30 and 35 l/d. Using HRT of 5.5 d as a baseline value, it correspond to 20%, 33% and 44% reduction in HRT respectively. Reduction of 20% and 33% in HRT leads to 21% and 7 % increment in litres of biogas per kg COD respectively while a reduction of 44% in HRT results in 34% decrease in biogas production. Even though, the higher the organic load, the smaller the digester volume can be chosen. It can be concluded from the results shown that increasing the organic volume load decreases the HRT and this have effect on the gas production especially at extremely high liquid flow rate (extremely low HRT). This is further illustrated by figure 6.29 where profiles or trends of specific biogas and methane production with respect to COD and BOD as a function of HRT are shown.

The trend lines in both figures indicate that, gas production is affected at extremely low and high HRTs.

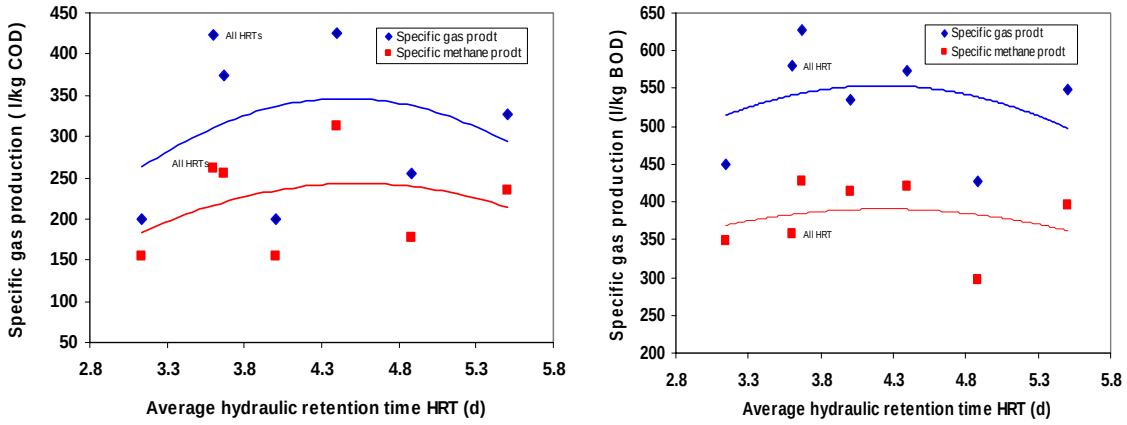


Figure 6.29. Specific gas production and the HRT.

HRT and removal rates in the methane reactor. Taking into account the experimental setup of a completely stirred reactor and the procedure used in the experiments, the hypothesis of complete mixture for both the liquid and the solid phases can be established.

According to Borja et al. (2003), the volumetric rate of substrate uptake (total COD) or substrate removal rate can be obtained from the equation:

$$-(rCOD) = \frac{(COD_o - COD)}{(HRT)} \qquad 7.6$$

Where COD_0 is the incoming total COD concentration or total COD concentration in the reactor, COD is the effluent concentration and HRT is the HRT. The minus sign in *r*COD only has physical meaning, and it indicates that COD concentration diminishes when increasing the HRT.

The variation in the substrate removal rate is presented in figure 6.30.

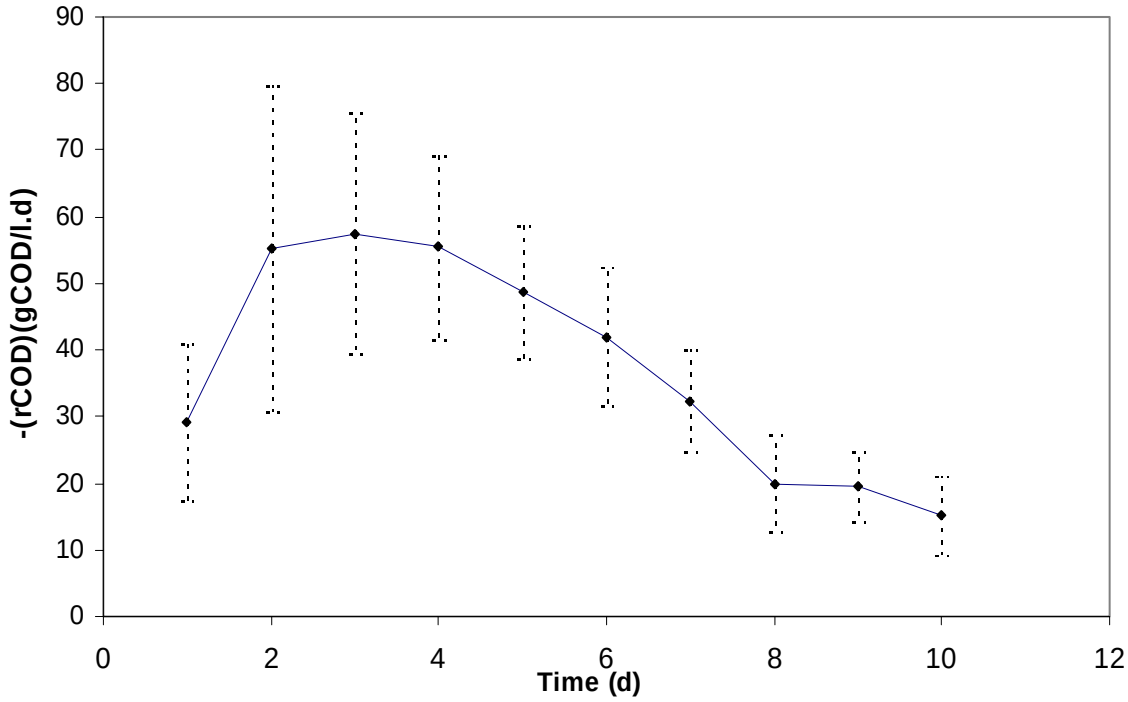


Figure 6.30. Variation of the substrate removal rate, rCOD (gCOD/l.d) as a function of operational time.

From figure 6.30, removal activity was observed to be very high during the early stages of the process where also the influent strength is high and then levels down to the end of the experiment. On an average, 38±19 gCOD/l.d removal rate was achieved with minimum and maximum values of 8.1 and 86.79 gCOD/l.d respectively.

HRT of the methane reactor and the effluent quality. The concentrations of the effluent liquid is presented in figure 6.31. It can be seen that the VOS concentration in the effluent exiting the methane reactor were far higher than that of the COD concentration as demonstrated in the figure 6.31. The data illustrates that COD removal did not show significant changes by increases in HRT but the effect was much pronounced in VOS removal from the methane reactor (slurry washout). To remove the effect of sludge influence on the COD of the effluent exiting the methane reactor, the sample was centrifuged first before analysis which resulted a reduction in COD concentration of the effluent. Centrifugation of effluent samples was carried out to remove sludge material before determination was done and this led to approximately 84% reduction in the COD concentration.

On the average, the COD of the exiting effluent was 0.54±0.26 gCOD/l which is equivalent to an average concentration of 536±260 mg/l, while that of the VOS was 3.25 ±1.3 g VOS/l. This is an indication of a probable slurry wash out which is evident in figure 6.31.

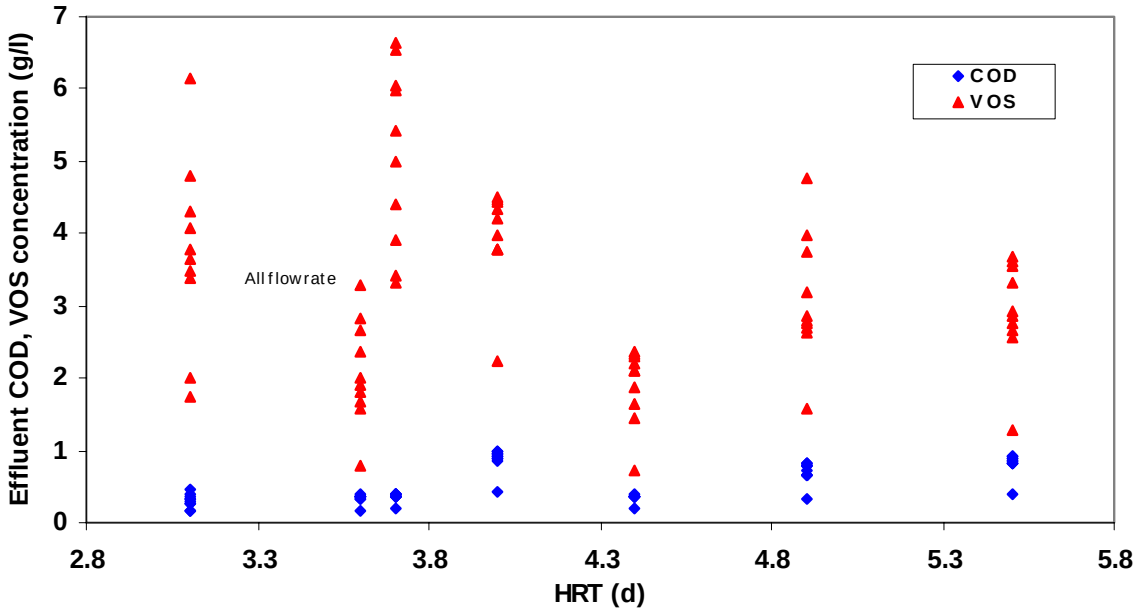


Figure 6.31. Concentrations COD and VOS of the exiting effluent of the methane reactor.

Impact of hydrolysis product on gas production. Cumulative biogas and methane production of the various experiments carried out at different flow rate of water (dilution) are presented in figure 6.32 and figure 6.33. In addition, the specific biogas production as a function of operation time at various HRT imposed on the hydrolysis reactor is given in figure 6.32.

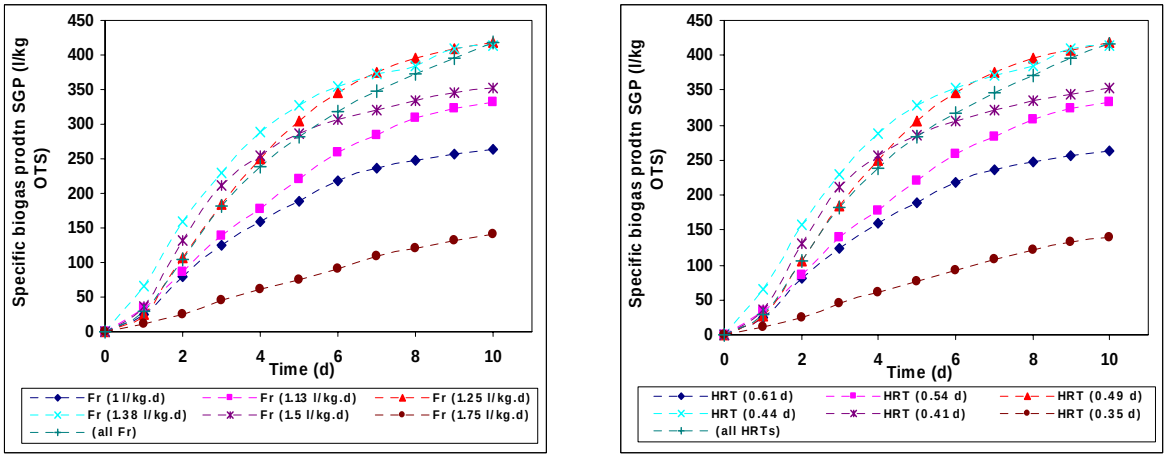


Figure 6.32. Specific biogas production as a function of operation time at different water flow rate regime to hydrolysis reactor and its corresponding HRT.

It was observed that, biogas production were highest for water flow rate regimes of 1.25, 'all flow rate' and 1.38 (L/kg input waste.d) delivered to the hydrolysis reactor leading to the leaching of soluble organic matter as COD.

The specific biogas and methane production rates expressed as per unit mass of dry matter were 418, 417 and 413 l biogas/kgOTS and 306, 257 and 286 l CH_4/kgOTS respectively. However, these trend of gas production is directly proportional to the leached COD and its quality from the hydrolysis reactor. The leached COD which is partly dependent on the flow rate and for that matter operating conditions imposed and the characteristics of the waste.

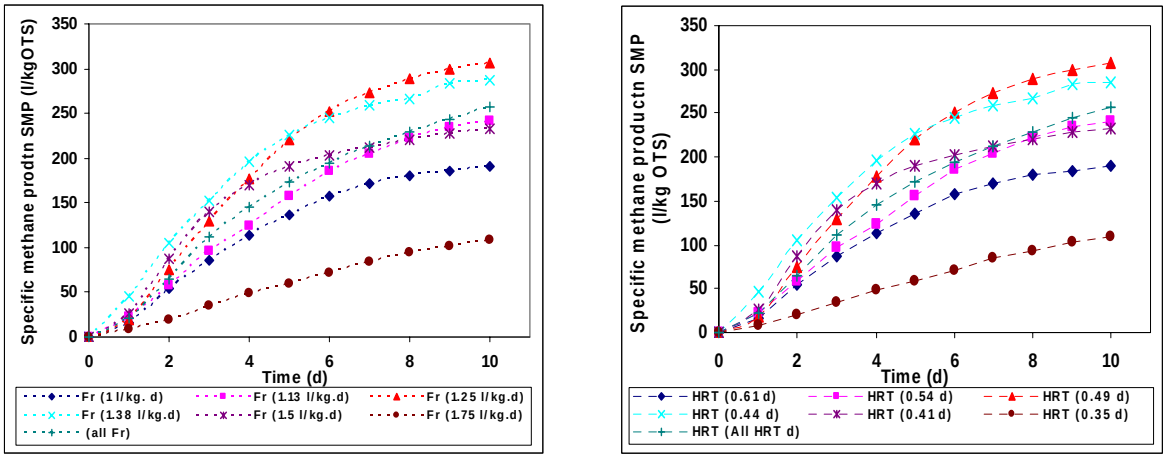


Figure 6.33. Specific methane production as a function of operation time at different water flow rate regime and corresponding HRT in hydrolysis reactor.

Effect of conductivity (salt) on biogas production. A profile of the conductivity and the pH as a function of operation time for the various experiments with their dilution rate is presented in figure 6.34.

From the data, it was observed that the effluent liquid pH and conductivity showed values higher compared to the influent liquid entering the methane reactor. On the average, the pH of the effluent liquid is 6% higher over the influent concentration. Similarly, on the average, the conductivity of the effluent liquid exiting the methane reactor is 24% higher than the conductivity of the influent liquid. The increase in value of conductivity after treatment may be due to accumulation of precipitation of salts from the leachate influent which satisfies the hypothesis that the double-stage treatment facilitates the solubilization and removal of metals from the waste.

AD with recirculation of process water leads to the enrichment with salts, therefore, occasionally, the process water has to be purged or diluted with fresh water to avoid inhibition (Ecke, 2000).

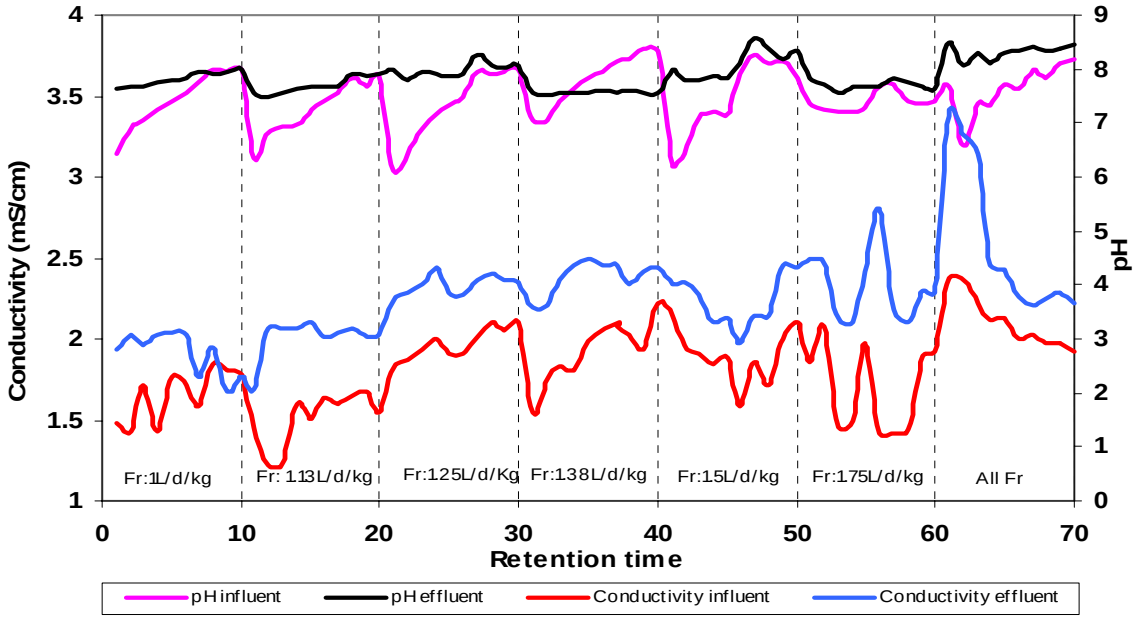


Figure 6.34. Conductivity and pH of the influent and effluent of the methane reactor as a function of operation time. The broken lines separates each experimental condition from the other.

Effect of conductivity on gas production was analysed through a simple scatter plot shown in figure 6.35.

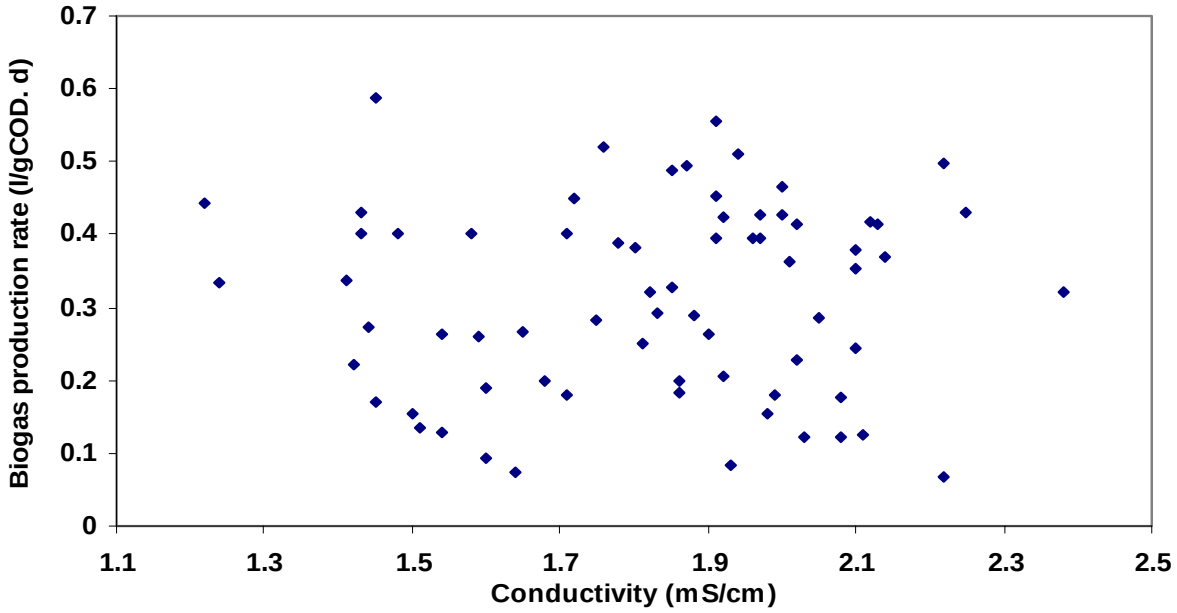


Figure 6.35. Specific gas production and the effect of salt as conductivity.

The salt content referred to as conductivity was observed to have no effect on the average biogas yield. This fact is illustrated in figure 6.35 as there appears to be no correlation between the two variables.

6.3.4 Evaluation of the reactor set-up and the anaerobic digestion of UMSW

Generally, it can be deduced that, the treatment approach of the UMSW using the double stage digester was a success. It was realized that, the UMSW waste can be hydrolysed at a degradation rate of 4.2±19% (dry matter). On a wet mass basis, reduction of 30±19% was achieved. However, significant amount of biogas with very high methane quality was produced. Therefore, all of these results indicates that anaerobic digestion is a practical and promising alternative for the treatment of UMSW before landfilling. Besides this, an average of 42.3±13.2% OTS of the organic matter added to the reactor was degraded during the anaerobic digestion of the UMSW at mesophilic temperature. The study also clearly demonstrates the progressive adaptation of the biomass to increase in substrate concentration, as well as a gradual increase in the methanogenic activity of the anaerobic sludge with the advance of the experiments.

The microaerobic technique applied in the hydrolytic stage proved to be effective in enhancing quick hydrolysis without any observable loss of COD through methanogenesis. Sand particles usually settled at the bottom of the reactor, occasionally this particles causes blockage of pumps and valves delivering liquid and this did pose much problems. Foaming did not occur and that was a big advantage for the treatment process. Ammonia concentration did not also pose any problem as it was always far less the threshold for inhibition. The natural buffer system was good to offset any observable treat from low pH. The natural buffer system was achieved synergistically by the inter recirculation process water exiting the methane reactor to the hydrolysis reactor and the intra recirculation of leachate within the hydrolysis. It was observed that the methane reactor was far capable in treating high concentrations of leachate coming from the hydrolytic reactor. The buffer system and its cooling characteristics was found to be necessary since the waste dealing with comes from different source.

The slurry bed used was found to be effective in treating the COD laden liquid from the hydrolysis. Though, biomass retention scheme was employed such as opposite movement of influent and effluent and the use of a ‘siphon’ to prevent slurry washout, occasionally, there is slurry wash out at high water flow rate regimes. In spite of the retention scheme used, from the COD and VOS values of the effluent determined indicates there is high amount of slurry washout.

6.3.5 Evaluation on the process

During the first 2 days of leachate recycling, rapid acidification in the hydrolytic stage was observed in terms of pH, COD and OA levels. This was consistent with other studies that a leachate recycle reactor goes acid quickly. Dissolved material as COD rapidly increased up to 50% (from 5.8±1.9 to 11.77±3.7g/l) for the first two days, while total OA increased from 35±12 g/l to over 71± 24g/l in the first 2 days. Further leachate recycling did not give significant increases in both COD and OA concentrations (i.e. days 2-8 for both COD and OA concentrations). It seem that the waste materials in the hydrolytic reactor had been acidified well in two days. Wang et al. (2002) reported similar findings about COD and OA removal within 3 days during the first stage treatment of canteen waste.

On average, degradation and leaching rates of 42±13% (OTS) and 51±8% (COD) respectively were achieved at the first stage. It was realized that degradation and leaching rates were both affected by water flow rate regimes especially at extremely low and high flow rates. Hofenk et al. (1984) confirms that at higher water to waste ratios, the concentration of the solubilized material such as OA and COD becomes unnecessarily low (i.e. < 5 g COD/l). On the contrary, for lower water to waste ratio, solubilized effluents from the hydrolytic reactor may have COD concentrations ≥50 gCOD/l and a pH as low as 4.2. similarly, Christ et al. (1999) also reported that the organic load of the influent is significant for the loading of the process water.

For decision making, it was found out that, a minimum leaching and degradation rates of 59 and 52% respectively could be achieved at water flow rate between 1.25 to 1.34 l/kg waste .d. The overall average pH for the entire experiment carried out was 7.14±0.55, a minimum of 6.1±0.49 and maximum of 7.7±0.24 were observed.

In the methanogenic phase, no serious problem regarding the reactor's performance with respect to pH was encountered. This was probably due to the slight dilution of influent in the buffer prior to their entering into the methanogenic phase. The effective biodegradation in the methane reactor in terms of COD, BOD and OA removal were in the ranges of (85-95%), (92-99%) and (94-99%) respectively. At the end of operation, the median methane reactor effluent COD, BOD and OA concentrations were 380 mg/l, 80 mg/l and 36 mg/l respectively. No significant methane production was detected in the hydrolysis stage, but when the feeding of the methane phase started, biogas with high methane content of 71% was produced. About 99% of the total CH_4 yield was from the methanogenic phase. Low methane production in the acidification phase indicated that no active methane fermentation was developed probably because methane reactor effluent could not bring enough methanogenic bacteria to the hydrolysis reactor or could be due to environmental factors. The methane reactor used in the test was similar to the UASB reactor in

that, biomass is retained in the form of sludge granules. However, biomass washout was dependent on the liquid flow rate into the methane reactor.

The biogas production rate is presented in figure 6.36. The trend looks similar to the daily COD production and the daily gas production presented earlier.

The highest biogas production rate of 1.3±0.53 m^3/m^3 reactor. day occurs within two and half days after the start of the experiment.

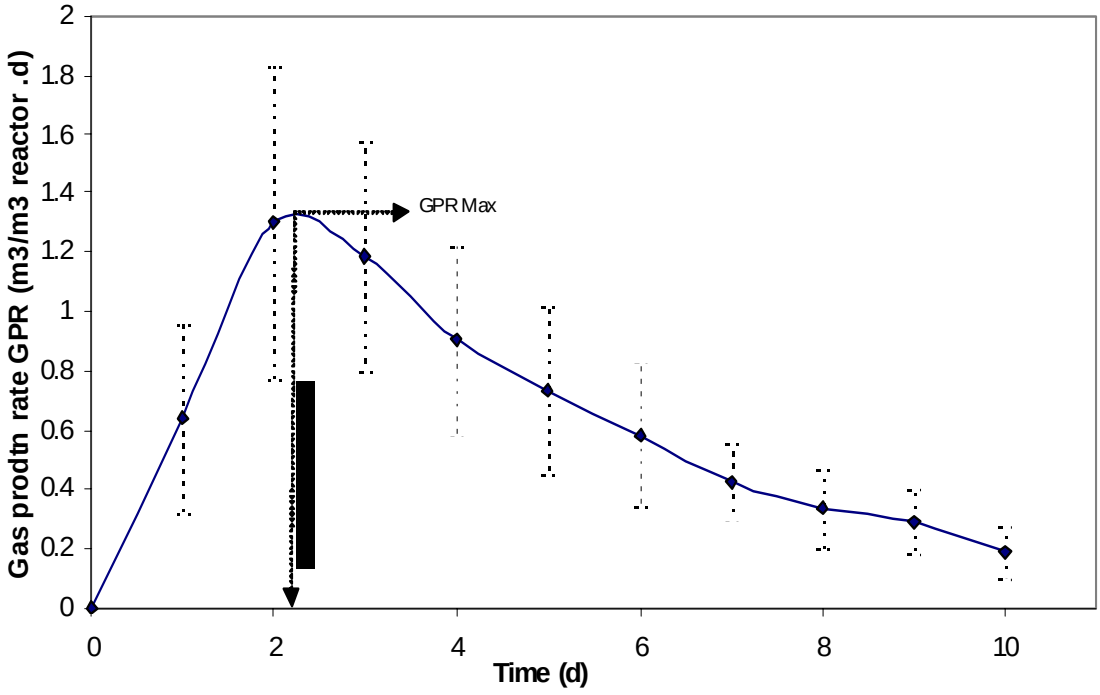


Figure 6.36. Biogas production rate as a function of the operational time in days.

An overall average biogas production rate of 0.66±0.4 m^3/m^3 reactor. day was observed at an average loading rate of 1.5±0.28 gCOD/l reactor.d and 0.75±0.25 gVOS/l reactor.d. Biey et al, (2003) operating multiple stage digester treating vegetable fruit garden waste at 30°C reported biogas production rate of 1.2m^3/kg VS of fresh waste when loading rate of 4.1 kgVS/m^3 reactor. day was applied.

The average specific gas and methane production graphs are presented in figure 6.37. An overall average values of 334±102 and 232±66 L/kg OTS for biogas and methane respectively were obtained. Vieitez et al. (2000) reported total biogas of 340 l/kg initial substrate VS, or 170 l/kg of methane per kg of initial VS in a two-phase leached bed biomethanization of organic rich MSW.

Furthermore, the system achieved a 54% VS reduction on weight percent basis which represents a destruction of almost 100% of the biodegradable fraction of the feed.

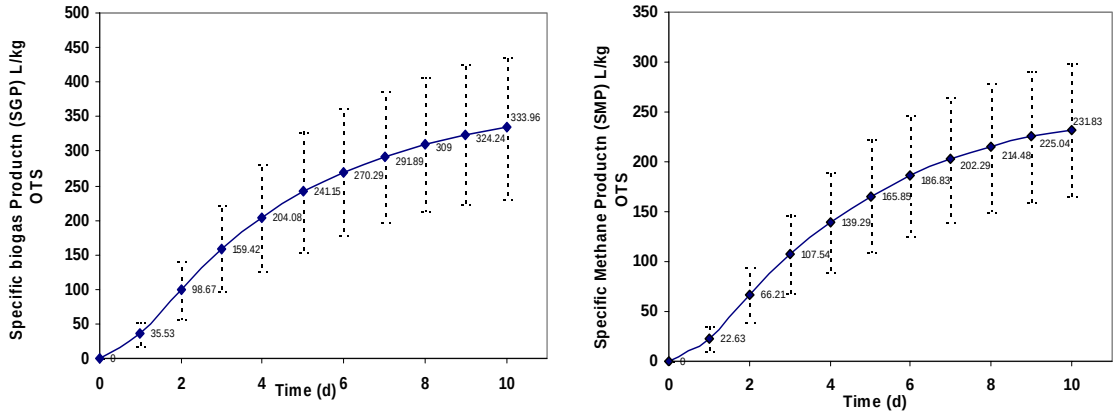


Figure 6.37. Average specific biogas (SGP) and methane (SMP) production within a standard deviation as a function of operation time.

A summary of biogas and methane production expressed in terms of different substances are presented in table 6.9.

Table 6.9. Specific gas production with respect to solid material input for hydrolysis and input leachate material

Parameter	Mean	S.D	Median	Min	Max
SGP* (l/kg OTS)	334	102	353	140	418
SMP* (l/kg OTS)	232	66	241	109	307
SGP (l/kg COD-Hydrolysis)	404	164	358	229	654
SMP (l/kg COD-Hydrolysis)	284	101	263	178	432
SGP (l/kg COD-input)	315	99	326	199	426
SMP (l/kg COD-input)	221	61	235	155	313
SGP (l/kg BOD-input)	577	142	574	426	861
SMP (l/kg BOD-input)	401	86	399	296	570

*SGP and SMP Specific gas and methane production respectively.

Yields of the overall system were quite good in terms of the specific gas production (SGP). (This parameter is given in four units, two referred to the volatile solids (COD and BOD) fed to the methanogenic reactor and the other two referred to the volatile solids (OTS-solid material and COD) fed to the system.

6.3.6 Conclusions

The double-stage anaerobic batch reactor systems for UMSW digestion were operated at 30±2^{o}C for the first stage and 38±2 ^{o}C for the methane stage for operation time of 10 days. The fermentation products from the two hydrolysis reactors were degraded by a separate

methanogenic reactor. This shows that the reactor arrangement is effective and efficient for the conversion of biodegradable organic fraction of the UMSW to biogas. On an average, treatment efficiencies of 42±13% OTS and 51±13% COD were removed in the first stage, while 90±6% total COD reduction was achieved in the methane reactor. The first-order kinetic model applied to predict the solid waste degradation for the first phase reactor gave an average hydrolysis rate constant of 0.15±0.08 day^{-1}. This is an indication that hydrolysis was the rate-limiting step in the anaerobic fermentation of the UMSW. The linear correlation between COD load removal and COD volume load indicates that the volume was not a limiting factor in these tests. Therefore, it is likely that the waste loading rate could be further increased because of the high treatment capacity of the methane reactor. The slurry bed methane was very efficient but involves a lot more supervision as stirring need to be regulated well to give ample time for slurry settlement before feeding. This would avoid simultaneous stirring and feeding which usually leads to slurry washout. This means that the slurry bed methane reactor can be used repeatedly with performance improvement. However, a fixed bed could be more appropriate yielding an equal or more production of biogas with less supervision.

Leachate recycling in the hydrolytic reactor is a fast way for effective hydrolysis and acidification of the UMSW. Removal of OA in an active methanogenic reactor is a built-in mechanism for prevention of system instability. Storage of the leachate from the hydrolytic stage in a buffer tank causes a form of OA dilution prior to the methane reactor.

This feature of the reactor set-up makes pH controlling unnecessary. Other advantages of the reactor set-up system used over other designs for anaerobic digestion of organic solid waste is that, there is no need all the time to add excess fresh water, to mix solid, and to treat wastewater produced during the process since the wastewater could be reused over and over again. The double stage batch process for the treatment of UMSW appears to be technically feasible at its current state of application. The double stage system can be further developed into an effective and efficient way to enhance waste stabilization prior to landfillling or in operated bioreactor landfills.

6.4 Solid Retention time and the treatment process

6.4.1 Evaluation on the process

Among the objectives to be achieved at this stage are, obtaining degradation of particulate organic matter in a shortest possible time and secondly to produce as much biogas as possible. Therefore, this experiment was carried out to determine degradation rate at and gas production at 7, 10 and 14 days solid retention time and as well for the overall process in order to make a

decision on the appropriate shortest SRT for the entire treatment process. The essential parameters measured for decision making are shown in table 6.10.

Table 6.10. Characteristics of the measured parameters

SRT (d)	OTS removal (%)	Leaching rate of COD (%)
7	35±1.8	43±1.3
7 days after (14 days)	24±0.8	32±0.5
10	44±3.6	50±0.9

From the results obtained, there was 16% additional degradation in OTS from 7 days to 10 days and 15 % for leaching of organic matter. The additional degradation and leaching rate increment from the 10th day to the 14th day were 12% and 10% respectively. Similarly, the gas production rate was also analysed and presented in figure 6.38 and figure 6.40. From figure 6.38, the amount of gas production reached 86% on the 7th day and 95% on the 10th day. From the 7th to the 10th day, there was 11% increment while from the 10th to the 14th day only 5% increase in the gas production.

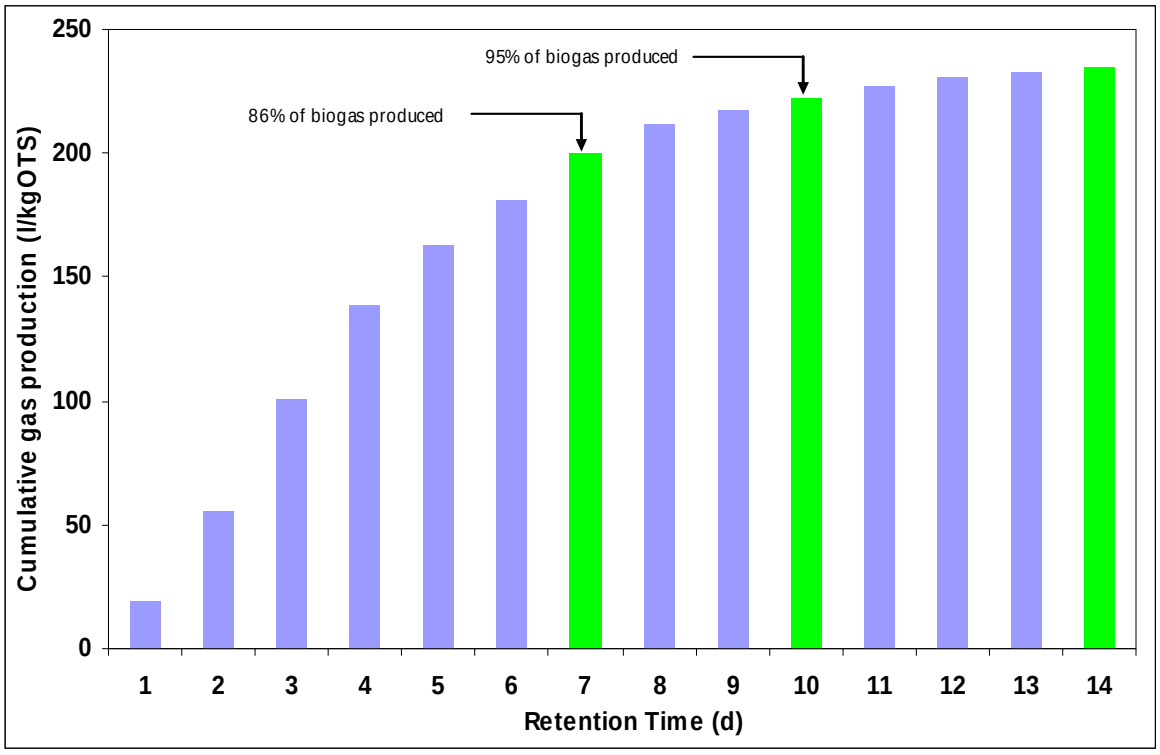


Figure 6.38. Cumulative biogas production as a function of operation time.

From figure 6.39, it can be deduced that, the biogas production was insignificant after 10 days of operational time with daily biogas production rate less than 6 l/d. After 10 days of operation there

was an end to a major biogas production activity due to significant reduction of COD from the hydrolysis reactor.

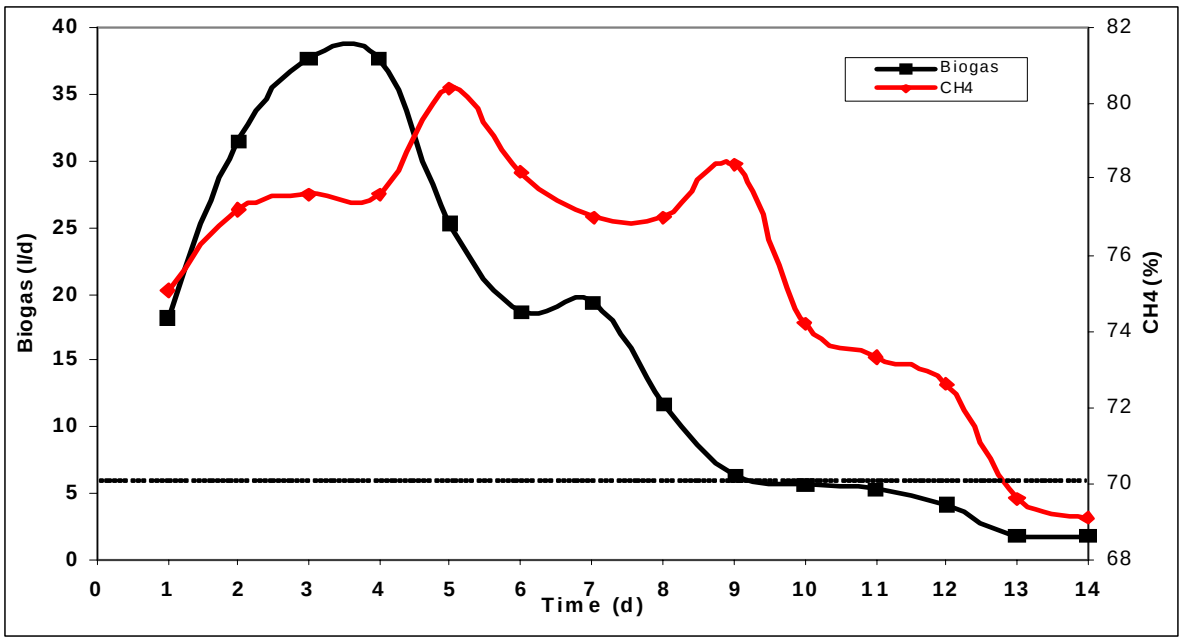


Figure 6.39. Daily biogas production and methane quality as a function of operation time. The broken lines illustrates the amount of gas production after 10 days of operation.

6.4.2 Conclusions

The results presented gives a very fair idea about the SRT retention appropriate for the treatment of the waste. By 10 days of active digestion, a minimum of 44% of the total input organic total solid has been degraded and 50% of COD has been leached out. Average concentrations of COD and OA by 10 days of digestion were 4054±831mg/l and 726±52 mg/l respectively. Further leachate recycling did not give significant increases in both COD and OA concentrations (i.e. days 10-14 for both COD and OA concentrations). Concentrations of COD and OA concentrations between 10 and 14 days were 1511 mg/l and 42 mg/l respectively. It seem that the waste materials in the hydrolytic reactor had been well acidified in 10 days. Biogas production was highly significant by 10 days of methanogenesis of the leachate from the hydrolysis yielding 95% of the total biogas of the entire process.

6.5 Temperature and hydrolysis of particulate matter

These experimental run attempted to investigate the influence of temperature in the hydrolysis reactor leading to the production of fermentation products.

The trend shows the variation among the three digester temperature used. As a result of the recirculation and leaching out of solubilized materials, the highest concentration of pollutants was achieved after three days of operation. On day two, the concentration was at its highest peak and after 3 days there was no significant additional increase of COD. The COD trend is in conformity with the other pollutants like OA, TS, VOS. Table 6.11 represents the effect of different operating temperature in terms of pollutant cumulative load production expressed as g/kgOTS. The parameters presented include COD and OA. Degradation and OA/COD ratio as percentages are also presented. It is important to note that the first-stage mechanism (dilution and liquid recirculation) regarded as optimum condition was maintained for the test conditions.

Table 6.11. Summary of essential parameters measured at the studied conditions.

Parameter	Ambient (26-28^{o}C)	30 ^{o}C	35 ^{o}C
COD/OTS (g/kg)	454±7.9	486±148	610±23
OA/OTS (g/kg)	112±10.9	135±50	169±4.3
Degradation (%)	35±0.9	35±2.0	35±4.0
OA/COD (%)	25±1.9	29±0.9	27 ± 0.8

NB: Values expressed as mean ± standard deviation.

In terms of COD, a total of 454±7.9 gCOD/kg OTS was removed at ambient temperature, while at 30 ^{o}C much higher leachate load was generated (489±148 gCOD/kg OTS), however at 35 ^{o}C brought the highest load of 610±23 gCOD/kg OTS. From the data, 7% of COD can be generated more when operated at 30 ^{o}C condition than in ambient temperature. However, when it is increased to 35 ^{o}C condition, 34 % of COD can be removed more using ambient condition as a baseline. To compare the COD produced between 30 ^{o}C and 35 ^{o}C conditions, 35 ^{o}C condition offer 26% increase over 30 ^{o}C condition. It means that operating the digester at 35 ^{o}C could generate higher leachate load of pollutants. This is because operation temperature at 35 ^{o}C could generate higher volume of leachate which definitely affects the leachate cumulative load to become high. Similarly, the other leached components such as OA at 35^{o}C showed identical trend but slightly lower than that of 30^{o}C. However, the degradation rate does not vary significantly across the tested conditions. The hydrolysis rate (OA/COD) indicated the highest fermentation product at 30 ^{o}C which was 29±0.9%, while at 35 ^{o}C and ambient conditions 27±0.8% and 25±1.9%.

6.5.1 Quality of leachate generated from the hydrolysis phase

Table 6.12. represents the most important parameters measured in the liquid phase of the hydrolytic reactor (concentrations of the raw samples) and their variation across the three temperature conditions (ambient, 30 ^{o}C, and 35 ^{o}C) include COD, OA, BOD, TS, VOS, pH conductivity and salinity.

Table 6.12a-6.12c. Summary of concentrations of the most important parameters measured during the time course of experiments at ambient (a), 30 ^{o}C (b) and 35 ^{o}C (c).

(a)

Parameter	Effluent mg/l				
	Mean	S.D	Median	Min	Max
COD	2465	1131	2090	1388	4950
OA	573	511	393	141	1676
TS	8342	1164	8074	7217	10265
VOS	2777	566	2557	2295	3714
Cond	2.26	0.12	2.31	2.08	2.42
Sal	0.98	0.13	1.0	0.60	1.1
pH	7.52	0.23	7.57	7.06	7.85

(b)

Parameter	Effluent mg/l				
	Mean	S.D	Median	Min	Max
COD	5193	2892	4715	1975	10890
OA	1627	1113	1456	150	3715
TS	7814	2035	6818	6280	11212
VOS	3177	1402	2689	2165	5580
Cond	2.17	0.09	2.15	2.05	2.30
Sal	0.97	0.08	0.95	0.9	1.10
pH	7.31	0.60	7.44	5.9	7.89

(c)

Parameter	Effluent mg/l				
	Mean	S.D	Median	Min	Max
COD	3511	2329	2693	1153	7510
OA	728	711	499	67	2166
TS	8053	852	7936	7172	9462
VOS	2383	685	2359	1743	3421
Cond	3.59	2.62	2.54	2.40	10.0
Sal	1.82	1.59	1.20	1.10	5.70
pH	7.57	0.36	7.43	6.97	8.15

At an ambient and 30^{o}C conditions gives a higher TS and VOS concentration (mg/l) over 35^{o}C where concentrations were lower. However, the conductivity at 35^{o}C appears to be higher (3.59 mS/cm) while at ambient and35^{o}C conductivity values were 2.26 and 2.17 mS/cm respectively. The pH values remain relatively the same except at 30^{o}C where there was slightly lower value of 7.31±0.60 compared to 7.52±0.237 and 57±0.36 respectively for ambient and 35^{o}C. Biogas production in the first-stage of the hydrolysis was insignificant. On average, 2.2±1.5%, 2.8±1.7 and 2.6±1.4% of methane production were observed for ambient, 30^{o}C and 35^{o}C respectively in the hydrolysis reactor.

The gas production profiles during methanogenesis are provided in figure 6.40 where the specific biogas and methane production are presented over the operation time.

The performance of the mesophilic methane reactor in terms of specific biogas and methane production can be evaluated by comparing the results among the three reactor conditions. It is important to point out here again that, the same temperature conditions of 38±2 ^{o}C was maintained for the methane reactor in all the temperature conditions imposed on the hydrolysis reactor.

Generally, the data presented suggests that the operation of the hydrolysis reactor at 30 ^{o}C produced quality fermentation products leading to the highest volume of biogas produced.

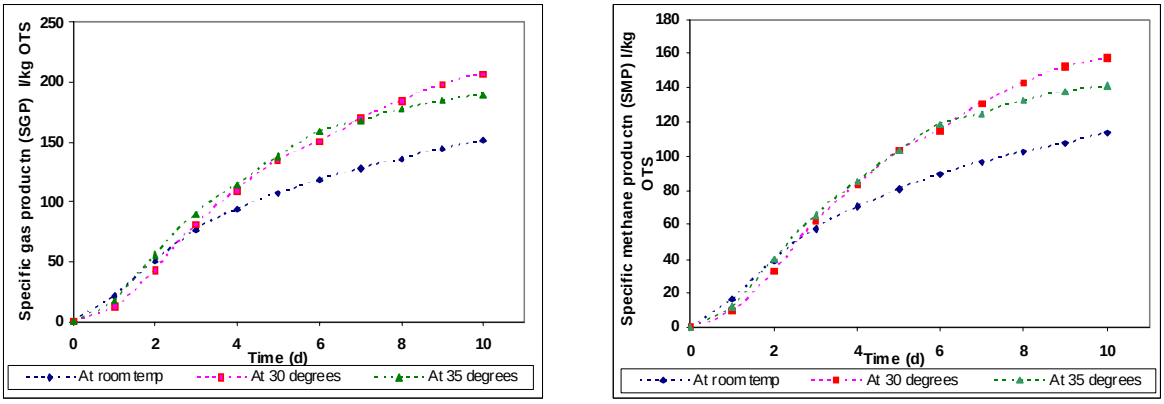


Figure 6.40. Specific biogas and methane production as a function of operation time.

In terms of biogas, a total of 150±50 l/kg OTS was produced at ambient temperature, while at 35 ^{o}C much higher biogas was generated (189±108 l/kg OTS), however at 30 ^{o}C produced the highest biogas of 206±63 l/kg OTS. From the data in figure 6.40, 26% of biogas can be generated more when operated at 35 ^{o}C condition than in ambient temperature. However, when it is at 30^{o}C condition, 27% of biogas can be produced more using ambient condition as a baseline. To compare the biogas produced between 30 ^{o}C and 35 ^{o}C conditions, 30^{o}C condition offer 8% increase over 35^{o}C condition. Similarly, in terms of methane production, a total of 113±25 l/kg OTS was produced at ambient temperature, while at 35 ^{o}C much higher methane was generated (141±45 l/kg OTS), all the same, at 30 ^{o}C produced the highest methane of 157 l/kg OTS. The differential in gas production could mean that operating the hydrolysis digester at 30 ^{o}C could generate higher quality COD load which resulted in the higher gas production.

6.5.2 Conclusions

The aim of these experiments was to determine how much of biogas is achievable under the three temperature conditions. In terms of COD, 35 ^{o}C in the hydrolysis brought the highest load of 610±23 g/kg OTS while, a total of 489±148 g/kg OTS and 454±7.9 g/kg OTS was removed at ambient and 30 ^{o}C temperature conditions. It means that operating the digester at 35 ^{o}C could generate higher pollutant load. The hydrolysis rate (OA/COD) indicated highest fermentation at 30 ^{o}C which was 29±0.9%, while at 35 ^{o}C and ambient conditions were 27±0.8% and 25±1.9% respectively. The hydrolysis rate at 30 ^{o}C reflected in the gas production by having the highest biogas and methane values. A total of 150±50 l biogas /kg OTS or 113±25 l methane /kg OTS was produced at ambient temperature, while at 35 ^{o}C much higher biogas was generated (189±75 l biogas/kg OTS or 141±45 l methane/kg OTS), however at 30 ^{o}C produced the highest biogas of

206±63 l/kg OTS or 157 l methane/kg OTS . From figure 6.40, 26% of biogas can be generated more when operated at 35 ^{o}C condition than in ambient temperature. It is also important to mention that, owing to the fluctuations in the composition of biowaste composition, a correlation between the some of the measured parameters and the conditions imposed could not be discerned. However, operating the digester at 30^{o}C in the hydrolysis and 38±2 ^{o}C in the methane reactor appears to be the best operating conditions under the study.

6.6 Effect of preprocessed substrates on anaerobic degradation

First of all, it has been as reported by Paven et al. (2000) and Lissen et al. (2001), the origin and the kind (composition) of organic solid has a significant influence on biodegradability and consequently on biogas yields. For instance, mechanically sorted OFMSW has very different biodegradability compared to source-sorted OFMSW (the latter has a higher digestibility).

Table 6.13 shows some of the main characteristics of the fresh waste and the hydrolysed liquid produced during the experimentation of the following quality of waste: Market waste (chopped to a size of 8-40 mm), Simulated waste (all sizes), Mechanically sorted (8-40 mm), Mechanically sorted (40-120 mm), Shredded Waste (8-40 mm), 'Ideal waste' or control (all sizes) and Manually sorted waste (8-40 mm).

The Mechanically sorted (8-40 mm), Shredded waste (8-40 mm) and Manually sorted (8-40 mm) had a solid content of 4.8, 3.4 and 3.3 kg OTS respectively which was significantly higher compared to source sorted market waste of 1.7 kg OTS. Such variation is expected since the former contains significant amount of paper and cardboard, and non degradable materials such as plastics which are completely absent in the market waste, and have contributed to the volatile solids. On the other hand, the simulated waste, ideal waste and the mechanically sorted waste (40-120 mm) shared similar trend of OTS values which are also relatively higher than the market waste. This variation is also due to the presence of paper and card board, and non degradable plastic fractions which are completely absent in the market waste.

Table 6.13. The most important parameters measured for the various waste fractions.

Parameter	Market waste	Simulated waste	Mech.sorted (8-40 mm)	Mech.sorted (40-120 mm)	Shred. waste (8-40 mm)	Ideal waste (all sizes)	Man.sorted (8-40 mm)
OTS (kg)	1.7±0.2	2.9±0.7	4.8±0.3	1.8±0.6	3.4±0.4	2.4±0.3	3.30±0.3
COD/OTS (g/kg)	885±2	468±25	441±53	796±284	712±133	640.1±23	837±18
OA/OTS(g/kg)	210±12	138±4	144±15	237±78	166±22	160±52	219±22
OA/COD (%)	24±0.3	29±0.9	33±0.5	30±0.9	21±5	20±0.5	26±3
OTS Degrad (%)	82±0.4	46±1.4	42±8	47±17	51±3	52±7	51±5

NB: Values expressed as mean ± standard deviation

With respect to degradation of the solid particulate matter expressed as percentage OTS removal, market waste gave the highest OTS removal rate of 82±0.4% while the removal rate for the rest of the substrate was between 42±8 and 52±7%. In terms of waste components, the market waste significantly differs from the municipal solid waste. The organic fraction of the market waste and UMSW were 95% and 65% respectively. The market waste exhibits higher volatile solids than the MSW and this correlate with its biowaste content. Therefore, as pointed out in table 6.13, more amounts of pollutants can be removed from the market waste than the UMSW. This points out the fact that the market waste is composed of more easily biodegradable organics than MSW. The lowest leachate load in terms of gCOD/kg OTS and degradation expressed as percent OTS was recorded for mechanically treated waste with component size of 8-40 mm.

This was not a surprise since the waste characteristic posed some problems during the hydrolysis. The small sizes of the feed material which consisted of more sandy particles which did not contribute anything to the leachate load. In addition, toxic substances (high alkaline or spilled chemical) may be concentrated and this could result in inadequately digested particulate material. Therefore, there is a need for an additional approach in treating this waste fraction type such as combined digestion with higher fraction waste (40-120mm). Also, an alternative is by employing an additional facility to remove the sandy fractions before digestion. An observation made was that materials such as plastics, inert and garden waste in the untreated waste provided the structure necessary to allow leachate, which is spread continuously over the waste mass during the process, to permeate it during the digestion process. But the disadvantage is that, large fractions of plastics and cans traps a lot of leachate which goes unaccounted for and thus, reduces biogas production.

6.6.1 Correlation between specific pretreatment and release of organic components

Aiming at the quantification of organic components readily available for degradation, the release of organic components into the solution was measured as COD during pretreatment as summarized in table 6.13. High COD can occur for one main reason, i.e., dissolution of organic components through new generated surfaces as a result of the pretreatment.

Nevertheless, the leached product gCOD per kg OTS for the market waste supercedes the rest of the substrate types. The rest of the waste that was used had leachate COD as per kg OTS in the following decreasing order: Manually sorted (8-40 mm) > Mechanically sorted (40-120 mm)>Shredded waste (8-40 mm) > Ideal waste (all sizes) > Simulated waste > Mechanically sorted (8-40 mm). Considering the fermentation products formed from the hydrolysis in terms of gOA/kg OTS, mechanically sorted (40-120 mm), manually sorted (8-40 mm) and market wastes presented similar highest OA load of 237±78, 219±22 and 210 gOA/kg OTS respectively where the variation between them was not more than 12%. Similarly, the degree of hydrolysis (OA/COD) were similar, 30±0.9, 24±0.3 and 26±3% respectively.

6.6.2 Quality of leachate generated during hydrolysis phase

Table 6.13a-6.13g presents the effect of different operating substrate conditions on pollutant cumulative load expressed in mg/l from the hydrolysis reactor. The parameters presented include COD, OA, BOD, TS, VOS, Conductivity, pH and salinity.

Table 6.13a-6.13g. Summary of the leachate characteristic during the hydrolysis of the fractions

(a) Mech sorted-8-40 mm

Parameter	Effluent mg/l				
	Mean	S.D	Median	Min	Max
COD	9398	3690	9420	4278	16000
OA	2783	1252	2436	813	4970
TS	9751	2084	9798	7619	12992
VOS	5089	1056	4964	3756	6691
Cond	2.09	0.09	2.11	1.97	2.20
Sal	0.91	0.06	0.9	0.85	1.0
pH	6.80	0.44	6.85	5.98	7.45
COD:OA	3.56	0.81	3.25	2.6	5.25
COD:VOS	1.62	0.60	1.83	0.91	2.29

(b) Manually sorted

Parameter	Effluent mg/l				
	Mean	S.D	Median	Min	Max
COD	11117	2720	10885	5825	16150
OA	2911	553	2911	1493	3392
TS	8499	1813	7800	7241	11666
VOS	5428	2064	4549	4159	9069
Cond	2.24	0.12	2.24	1.99	2.44
Sal	1.0	0.08	1	0.8	1.11
pH	5.47	0.23	5.52	5.1	5.73
COD:OA	3.9	1.03	3.90	3.14	6.46
COD:VOS	2.28	0.33	2.29	1.77	2.62

(c)Market waste (source sorted)

Parameter	Effluent mg/l				
	Mean	S.D	Median	Min	Max
COD	6013	3193	5433	2975	13190
OA	1372	904	1371	278	3168
TS	7489	1881	7121	6071	10707
VOS	3905	1616	3561	2690	6645
Cond	2.41	0.11	2.42	2.22	2.58
Sal	1.09	0.07	1.10	1.00	1.20
pH	7.06	0.77	7.22	5.19	7.74
COD:OA	5.29	2.26	4.18	3.62	10.70
COD:VOS	1.47	0.33	1.55	1.1	1.94

(d) Shredded waste

Parameter	Effluent mg/l				
	Mean	S.D	Median	Min	Max
COD	9907	5319	8331	4742	18640
OA	2228	1621	1894	321	4819
TS	9318	2369	7961	7287	12824
VOS	4549	1720	3378	3262	7005
Cond	2.16	0.08	2.15	2.02	2.31
Sal	0.98	0.10	0.9	0.9	1.20
pH	7.06	0.69	7.29	5.72	7.91
COD:OA	5.89	3.37	4.78	3.87	14.78
COD:VOS	2.07	0.61	2.35	0.89	3.66

(e) Ideal waste (Control waste)

Parameter	Effluent mg/l				
	Mean	S.D	Median	Min	Max
COD	7734	4733	7734	2200	16855
OA	1515	723	1515	393	2458
TS	8017	2272	8107	5585	11205
VOS	3373	1860	3925	969	5680
Cond	2.59	0.31	2.59	2.19	2.97
Sal	1.43	0.34	1.43	1.0	1.90
pH	6.74	0.95	6.74	4.72	7.60
COD:OA	4.97	1.21	4.97	3.34	6.86
COD:VOS	2.20	0.54	2.27	1.68	2.97

(f) Simulated waste

Parameter	Effluent mg/l				
	Mean	S.D	Median	Min	Max
COD	4304	2805	3620	1505	10430
OA	1193	949	983	190	3182
TS	7267	2219	6532	5524	10481
VOS	3591	1835	2987	2149	6242
Cond	2.38	0.10	2.35	2.3	2.6
Sal	1.1	0.07	1.1	1.0	1.2
pH	7.08	0.58	7.18	5.71	7.71
COD:OA	4.4	1.52	3.7	3.3	7.9
COD:VOS	1.3	0.3	1.3	1.0	1.7

(g) Mech sorted (40-120) waste

Parameter	Effluent mg/l				
	Mean	S.D	Median	Min	Max
COD	5283	2244	5406	1798	9190
OA	1599	939	1594	154	3291
TS	7814	2035	6818	6280	11212
VOS	3177	1402	2689	2165	5580
Cond	2.20	0.07	2.14	0.09	2.29
Sal	0.97	0.07	0.95	0.09	1.10
pH	7.24	0.46	7.23	6.28	7.78
COD:OA	4.28	2.67	3.56	279	11.67
COD:VOS	1.7	0.73	1.65	0.79	2.77

In terms of leachate concentration, the pretreated waste generally presented higher load concentrations relative to the simulated waste. Manually sorted gave the highest average leachate concentration of 11117±2720 mgCOD/l while the simulated waste gave 4304±2805 mgCOD/l. One of the factors that could influence hydrolysis process is the presence or availability of enzymes. But importantly, usually the amount of enzymes is not rate limiting in complex wastes (Hobson, 1987). This idea supports the fact that high hydrolysis yield could be achieved by using market waste substrate and control waste which agrees to the result of the experiment.

A pH profile during the hydrolysis of the various pretreated material as a function of operational time is presented in figure 6.41.

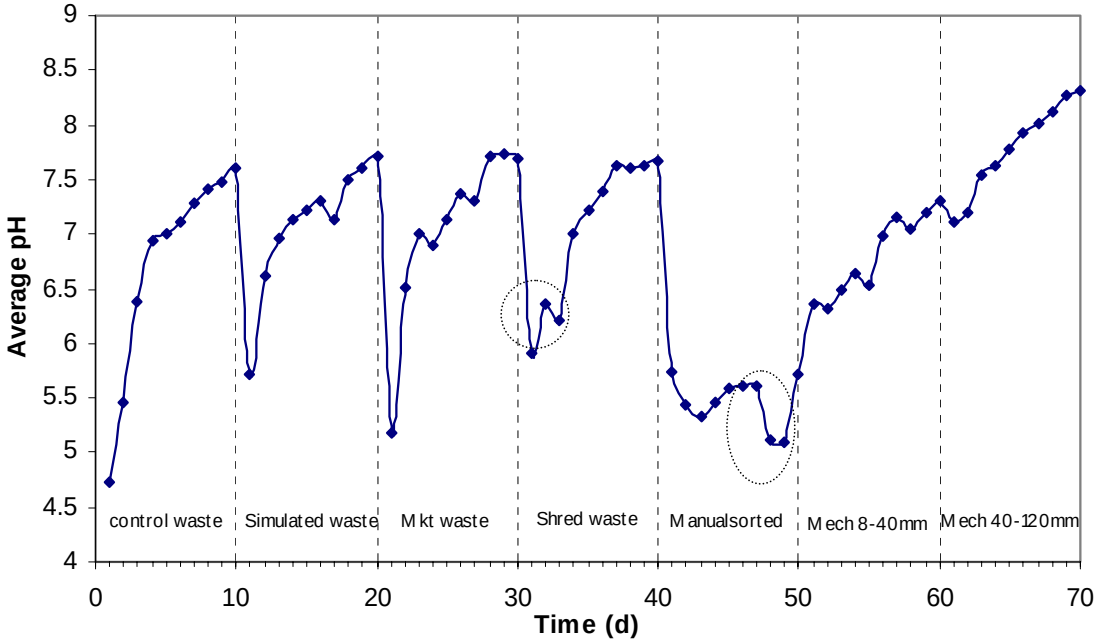


Figure 6.41. Hydrolysis reactor characteristics of the various fractions of input material. The vertical broken lines indicate the start and the end of an experiment.

Generally, pH decreases at the beginning of the entire test carried out due to release of organic acids. But the pH increased steadily to the end of the operational time. The control, the market and the manually sorted wastes offered the lowest pH starting values from as low as 4.7. There were some observations made (circled points on figure 6.41) during the hydrolysis of the sorted waste and the shredded waste. As a result of the physical characteristics of the pretreated waste, there was occasional stagnation of liquid on the waste bed difficult to leach through it. Therefore, this called for opening of the reactor in the course of the experiment to apply some amount of stirring to allow the stagnant liquid to flow through the waste to the bottom carrying along solubilized substances. The occasional correction of the reactor led to fluctuations in the pH profile, instead of steady rise. The stagnation effect was more pronounced in with the shredded waste. The pH profile for the mechanically sorted waste (40-120 mm) maintained continuously high pH values from the start to the end.

This may be a result of the presence of more alkaline materials in the feed. The specific biogas and methane production are presented in figure 6.42.

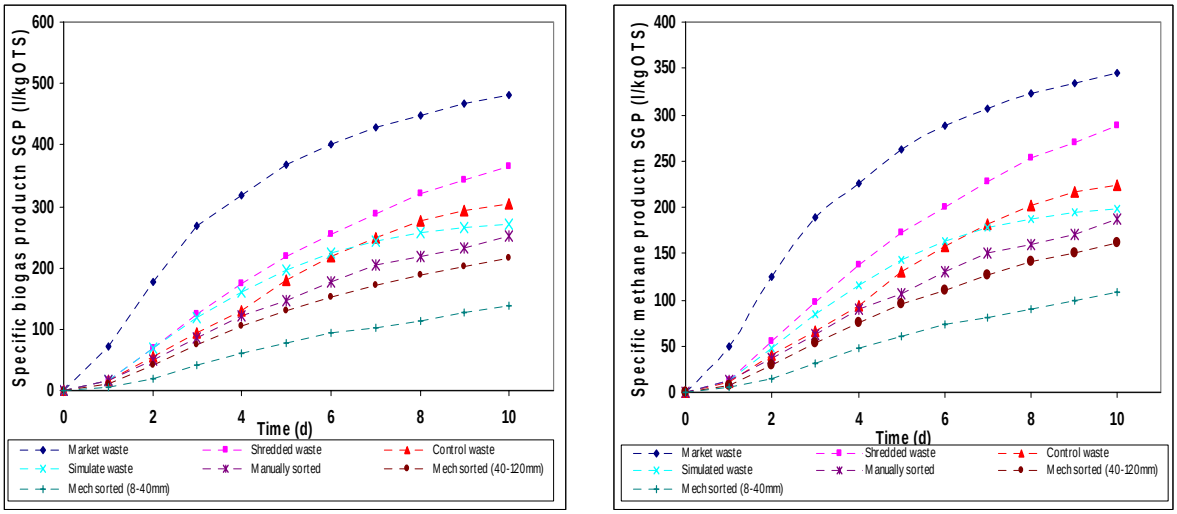


Figure 6.42. Specific biogas and methane production as a function of operational time

The aim of the pretreatment process before hydrolysis was to improve the biodegradability of the organic substrate and subsequent improvement of digester gas production. The most important increase was observed for some of the samples that were subjected to pretreatment before hydrolysis (e.g. source sorted market waste and shredded waste).

From the data provided in figure 6.42 the biogas production, market waste, a source sorted waste gave the highest biogas and methane production at 481 l/kgOTS and 345 l/kgOTS respectively. The lowest biogas and methane production were 138 l/kgOTS and 109 l/kgOTS respectively, resulting from the digestion of the mechanically sorted waste of size 8-40mm. The rest of the feed gave the following decreasing order of biogas production: shredded waste>simulated waste>control>manually sorted waste>mechanically sorted waste (40-120mm)>mechanically sorted waste (8-40mm). It is also important to mention here that, effectively, biogas yield in the solid waste digestion as such is much more dependent on waste composition than on process performance. According to Saint-Joly et al. (2000), the waste quality even at the same fermentation conditions, the biogas yield expressed per fresh waste or volatile solids can vary by a certain factor under normal conditions of temperature and pressure. So, the biogas performance does not characterize a process since it is deeply governed by waste composition. Bernal et al. (1992) reported that digestion of waste with high biodegradability like market waste could pose a problem as a result of production of more acids than the methane bacteria can convert. However, in the study, there was no observable organic acid inhibition, as a matter of fact a balance or more stable process was observed.

6.6.3 Conclusions

The conclusions that were drawn from these tests were the following:

The yield from the hydrolysis were much better when market waste (source sorted waste) was used. Percentage OTS removal was nearly two times greater and SGP was nearly two times. Another remarkable difference was the amount of leached substances measured as gCOD/kgOTS, which was highest for the market waste followed by the manually sorted waste. The mechanically sorted waste of size 8-40 mm registered the lowest. In general, it was observed that preprocessing of the feed material led to the release of more leachate load relative to the simulated waste. However, the percentage OTS removal of the pretreated feed material were comparable (except market waste) to that of the simulated waste with variation not more than 13%. Also, the difference in the degree of hydrolysis calculated as (OA/COD) were found not to be very significant. From the analysis, it can be concluded that, leachate removal process was more predominant than acidification especially when substrate particle size was reduced. Therefore, the reduction in particle size could enhance the leaching process. The yield from the control sample also stress the effect of the quality of the waste (the extent of freshness) has over the simulated waste. This also supports the fact that, the amount of enzymes is not rate limiting in complex waste, high hydrolysis yield could be achieved in control waste which agrees to the result of the experiment. Problems concerning stagnation of liquid on the waste bed of the manually sorted waste and that of the shredded waste were encountered, which call for an additional mechanism such as stirring to ensure smooth running of the process during the hydrolysis stage.

Gas production on the other hand, market waste, a source sorted waste gave the highest biogas and methane production at 481 l/kgOTS and 345 l/kgOTS respectively. The lowest biogas and methane production were 138 l/kgOTS and 109 l/kgOTS respectively, resulting from the digestion of the mechanically sorted waste of size 8-40mm. It was an observation that, the biogas production was much more dependent on waste composition than on process performance. Ammonia concentration was constantly monitored during the process and the concentration does not exceed 450 mg/l. Hence, ammonia inhibition does not occur in this system.

6.7 Overall summary of the pretreatment process using the double stage digester

The double-stage anaerobic batch reactor systems for the digestion proved to be effective and efficient for the conversion of biodegradable organic fraction of the UMSW to biogas with high quality methane content.

Effect of flow rates. Operating digestion systems at 30±2^{o}C for the first stage and 38±2 ^{o}C for the methane stage at an operational time of 10 days gave an optimum yields. It was observed that within ten days of active fermentation, the easily degradable organic matter was consumed and there was a significant reduction in the bulk volume of the mixed waste. The UMSW waste can be hydrolysed at a degradation rate of 4.2±1.3%.d^{-1}(OTS). On average, treatment efficiencies of 42±13% OTS and 51±13% COD were removed in the first stage, while 90±6% total COD reduction was achieved in the methane reactor. On wet mass basis, an average wet mass reduction of 30±19% was obtained. The trend obtained from the analysis demonstrates that lower leaching and degradation occurred at an extremely lower (high HRT) and higher (low HRT) liquid flow rate regimes. For decision making, it was found out that, a minimum leaching and degradation rates of 59 and 52% respectively could be achieved at water flow rate regimes between 1.25 to 1.34 l/kg waste .d. corresponding to HRT of 0.49 to 0.49 days.

The C/N ratio, pH profile and temperature gradients were comparable to that of traditional anaerobic digestion of MSW.

The first-order kinetic model applied to predict the solid waste degradation for the first phase reactor gave an average hydrolysis rate constant of 0.15±0.08 day^{-1}. This is an indication that hydrolysis was the rate-limiting step in the anaerobic fermentation of the UMSW. The linear correlation between COD load removal and COD volume load indicates that the volume was not a limiting factor in these tests. Therefore, it is likely that the waste loading rate could be further increased because of the high treatment capacity of the methane reactor. Gas production were favourable. On the average, 334±102 l biogas/kg OTS and 232±66 l methane/kg OTS were obtained. At optimum conditions, it was possible to achieve maximum specific biogas and methane yields of 418 l/kg OTS and 307 l/kg OTS respectively. There was no clear cut influence of HRTs on the biogas production, but there was a noticeable effect based on the volumetric liquid delivered and not from the influent strength.

Solid retention time. It was observed that the waste materials in the hydrolytic reactor had been well acidified in 10 days. Biogas production was also highly significant by 10 days of methanogenesis of the leachate from the hydrolysis yielding 95% of the total biogas of the entire process. Therefore, it is very economical to end the digestion process by 10 days instead of 14 days digestion period which gave rise to additional increase of 5% biogas.

Effect of temperature. In terms of COD, 35^{o}C in the hydrolysis brought the highest load of 610±23 g/kg OTS while, a total of 489±148 g/kg OTS and 454±7.9 g/kg OTS was removed at ambient and 30^{o}C temperature conditions. It means that operating the digester at 35^{o}C could generate higher pollutant load. But in terms of biogas, a total of 150±50 l/kg OTS was produced at ambient temperature, while at 35^{o}C much higher biogas was generated (189±108 l/kg OTS), however at 30^{o}C produced the highest biogas of 206±63 l/kg OTS. Similarly, in terms of methane production, a total of 113±25 l/kg OTS was produced at ambient, while at 35^{o}C much higher methane was generated (141±45 l/kg OTS), all the same, at 30^{o}C produced the highest methane of 157 l/kg OTS. The differential in gas production could mean that operating the hydrolysis digester at 30^{o}C could generate higher quality COD load which resulted in the higher gas production.

Yields from preprocessed feeding material. The yield from the hydrolysis was much better when market waste (source sorted waste) was used. Percentage OTS removal was nearly two times greater and specific gas production was nearly two times. Another remarkable difference was the amount of leached substances measured as gCOD/kgOTS, which was highest for market waste followed by the manually sorted waste. Gas production on the other hand, market waste, a source sorted waste gave the highest biogas and methane production at 481 l/kgOTS and 345 l/kgOTS respectively. The lowest biogas and methane production were 138 l/kgOTS and 109 l/kgOTS respectively, resulting from the digestion of the mechanically sorted waste of size 8-40mm. It was observed that, the biogas production was much more dependent on waste composition than on process performance. Problems concerning stagnation of liquid on the waste bed of the manually sorted waste and that of the shredded waste were encountered, which calls for an additional mechanism such as stirring to ensure smooth running of the process during the hydrolysis stage. Inclusion of a mechanical step to obtain a fraction between 40-120 mm would be recommendable. An observation was made, that materials such as plastics, inert materials and garden waste in the untreated waste provide the structure necessary to allow leachate, which is spread continuously over the waste mass during the process, to permeate it during the digestion process. But the disadvantage is that, large fractions of plastics and cans traps a lot of leachate which goes unaccounted for and thus, reduces biogas production.

7 CONCLUSIONS

The following can be concluded from this research:

The optimization design such as (1) intra and inter liquid recirculation, (2) Microaerophilic hydrolysis of the double-stage anaerobic batch reactor systems for the digestion proved to be effective and efficient for the conversion of biodegradable organic fraction of the UMSW to biogas with high quality methane content.

Effect of water flow rates (dilutions)

- Diluting the waste with an appropriate amount of water was essential for optimum hydrolysis of the UMSW.
- From the dilution process it was realised that both leaching and degradation rates were affected at extremely low and higher dilutions. Similarly, leaching and degradation rates were affected at extremely low and higher dilutions.
- The rate of removal of solubilized substances delivered to the methane reactor was linearly correlated with strength of the influent load. However, HRT seems to have effect on the biogas production at extremely low and higher HRT. From observation, liquid flow rate rather affect the reactor by washing out active bacteria responsible for material conversion. The reactor work best at higher influent strength.
- Biogas production was dependent on the quality of the influent liquid at an optimum HRT and at an appropriate liquid flow rate.
- Effects from inhibition substances such as ammonia and hydrogen sulphide were not observed.
- The C/N ratio, pH profile and temperature gradients were comparable to that of traditional anaerobic digestion of MSW.

Solid retention time

- The waste material fed to the hydrolytic reactor was well acidified in 10 days. Biogas production was also highly significant by 10 days of methanogenesis of the leachate from the hydrolysis yielding 95% of the total biogas of the entire process.

Effect of temperature

- Operating the digester at 35^{o}C could generate higher leachate load measured as gCOD per kg organic total solids. Ambient temperature generated the lowest leachate load.
- In terms of gas production, the leachate load from the digester operated at 30^{o}C produced the highest gas. However, it also indicates that the quality of the leached COD was more quality compared to that from the other conditions.

Effect of pretreatment on yield

- The most important increase was observed for some of the samples that were subjected to pretreatment before hydrolysis (especially source sorted market waste and shredded waste, and manually sorted waste).
- The yield from the hydrolysis was much better when market waste (source sorted waste) was used. A remarkable difference was the amount of leached substances measured as gCOD/kgOTS, which was the highest for market waste followed by the manually sorted waste.
- Problems concerning stagnation of liquid on the waste bed of the manually sorted waste and that of the shredded waste were encountered, which would require an additional mechanism such as stirring to ensure smooth running of the process during the hydrolysis stage.
- Gas production on the other hand, market waste, a source sorted waste gave the highest biogas and methane production. The lowest biogas and methane production were recorded from the digestion of the mechanically sorted waste of size 8-40mm.

8 SUMMARY AND TECHNICAL APPLICATION

The double stage dry-wet fermentation system employed in this study is capable for the treatment of putrescible refuse and leads to the achievement of the main goal outlined in the introduction of the thesis.

In considering commercial recovery of biogas from UMSW in a reactor treatment, it is important to assess the waste composition, which shows an expected high proportion of biodegradable organic components with corresponding high moisture content. Currently, the daily generation of UMSW in the Accra metropolis is 1800 tons, and this is increasing at a rate of 3.7% per year. The expected daily average of waste that would be delivered to the treatment facility at present is about 1,200 tons per day. By extrapolation, a yearly average of 438,000 tons of waste is expected to be conveyed to the facility. This amount of UMSW is economically sufficient to operate a bioreactor. Based on the amount of waste to be delivered per day, the size and the volume of the digester is determined. From a known predetermined SRT, each digester would be emptied after 10 days and refilled.

Basic calculations

- Current daily generation of UMSW in the Accra metropolis is 1800 tons.
- Average volume of UMSW collected in the Accra metropolis and transported to the landfill per day is 1200 tons which equals to 1200000 kg.
- For flexibility and cost effectiveness, 4 treatment facilities would be decentralised within the metropolis.
- This implies that, 300000 kg of the waste would be treated at each facility.

Assumptions

- From the laboratory study: the average %TS of UMSW is 22 and %VS of 65
- Temperature: 30±2^{o}C , C/N: 32 and HRT of the hydrolysis reactor being 0.5 d and SRT of 10 days.
- Average specific biogas and methane production were 334 and 232 l/kg OTS respectively. Methane quality of 68-72%.
- Desired TS of the diluted waste during hydrolysis is 10%.
- Percentage TS and OTS of the 300000 kg UMSW are 66000 kg and 42900 kg respectively.
- Assuming 42% of the OTS will be degraded which is equivalent to 18018 kg.
- Based on simple mass and water balance around the reactor, the volume of water to be added to achieve 10% TS is 360000 kg. Subsequent water need would be met by recirculating the same process water again.

- The volume of digester required for the treatment is approximately 370 m^3

Below is a flow chart (figure 8.1) illustrating the commercial application of the anaerobic digestion treatment facility (one demonstration plant) in Accra, Ghana.

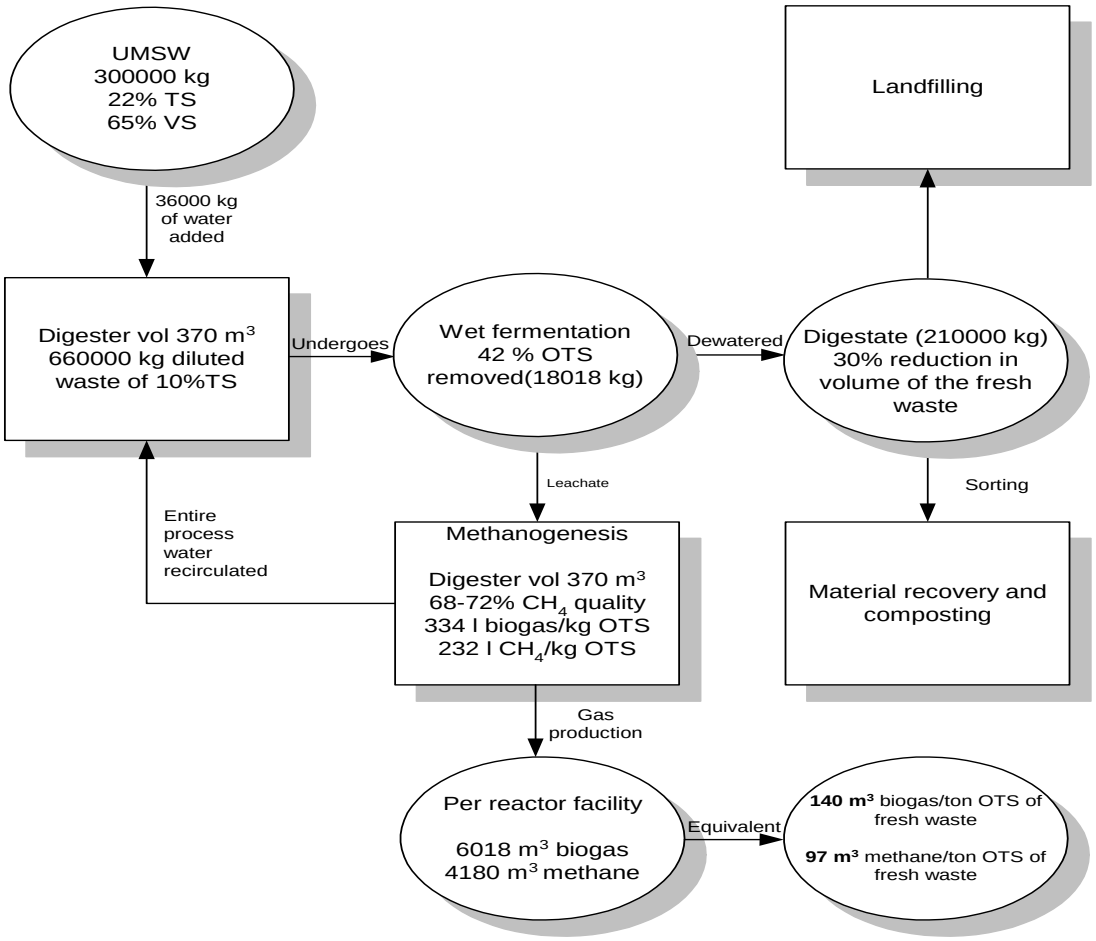


Figure 8.1. Commercial application of the double stage anaerobic digestion.

Therefore, for the 4 treatment facilities, a total amount of 24,072 m^3 biogas (30,000 KWh electricity) and 16,720 m^3 methane would be produced per day from 42,900 kg OTS. This implies that, 8,8 million m^3 (11 million KWh electricity) and 6,1million m^3 of biogas and methane respectively would be produced per year.

Future work. The following points are essential concerning the commercial applicability of the double-stage anaerobic digestion of unsorted municipal solid waste in Accra, Ghana.

- Carrying out of a pilot scale project.
- Conducting a statistical test that involves the real waste of the city of Accra.

9 OUTLOOK

The effective waste management practices and environmental improvement regulations in developed countries could be based on periods of economic development and environmental degradation they have gone through. It is an accepted fact that the standards achieved by the developed countries are simply unattainable by the developing countries in the short term. Nevertheless, some technological innovations such as the one employed in this study to pretreat UMSW, can be made available and is suitable to the conditions in the developing countries. This technology when applied could serve as a 'sink' for the large volume of waste generated in the metropolis to achieve a better environmental quality through innovative and cost effective waste management systems in the interim.

The following section consider the prospects of the anaerobic digestion treatment facility in the Accra metropolis. The assessment is presented from the technical, economic, environmental and the academic point of view.

Technical

The anaerobic digestion treatment facility proposed in this thesis is suitable for both sorted and unsorted waste. The result obtained from the laboratory experiment with UMSW confirms that the technology has the potential for implementation on a commercial level. The process has the possibility of pretreating the waste before landfilling and valuable end products such as biogas and compost would be obtained.

The building of the bioreactors could be made by using locally available raw materials (e.g concrete, wood, plastic linings) without the importation of expensive stainless steel reactor vessels. In addition, other essential components of the reactor, e.g. pipes, biogas collection facility/generator and liquid recirculation equipments are available on the local market.

The tropical temperature conditions seem appropriate for efficient running of the digester without any additional cost of heating the digesters. The digestate/stabilized material after digestion could be dried by spreading it on a level surface under tropical ambient temperature. The dried material could safely be sorted out to remove recyclable materials and the stabilized remaining organic material could be used as compost on agricultural fields. Alternatively, the overall digestate/stabilized material could be safely landfilled with little environmental consequences. Furthermore, the leachate remaining after its methane potential has been exhausted has a high nutrient level is good for bamboo cultivation. This same leachate can be reuse without or with little additional water saving cost on water.

Economic

The economic viability of such a treatment facility depends on the affordability of the treatment facility and the market for the products. The initial investment cost of this facility can be moderately high, but will pay-off at the end. However, the facility can be built using locally available material. Therefore it is economical.

The demand for biogas and digestate from the anaerobic digestion process in the Ghanaian society is encouraging and the market serves as a boost for the application of this technology. Most city residents at present use the liquefied petroleum gas as fuel for domestic cooking. Hotels, restaurants, boarding schools and chop bars use this gas for large scale food preparation and it is estimated to be cheaper than using hydroelectric power. The biogas that would be generated in the anaerobic digestion facility therefore has a high market value.

At the moment, it is difficult to ensure full cost recovery through waste user charges alone especially in the poor urban areas. For this reason, there is an urgent need for decision-making and financial improvement to meet budgetary constraints and to optimize solid waste management services. Preparation towards construction, operation and maintenance of anaerobic digestion facilities will ensure maximum environmental and social benefits. This will further ensure cost recovery and that is what the metropolitan authority must consider. At this point in time, the anaerobic digestion facility should be given every necessary consideration over the conventional dumping of waste. The biological treatment offers several benefits and is cost effective. Revenues could be derived from the sale of biogas and tipping fees collected could be used to fund the operation of the treatment facility.

Landfilling or dumping should be controlled and sufficiently expensive to make the moderate cost of an anaerobic digestion facility competitive.

Environmental

The strongest moral argument for adopting anaerobic digestion is that it gives the Accra metropolis an opportunity to effectively handle the waste generated. By doing so, it ensures an environmental and economic benefit which is an advantage. Since all of the products of anaerobic digestion have valuable end uses, there is no waste produced and therefore less use of landfills, where methane emissions create environmental damage. Other environmental benefits include improved water quality, renewable energy generation, reduced need for chemical fertilizers and enhanced air quality. The Rio Framework and the Kyoto Protocol concluded that reducing greenhouse gas emissions to the atmosphere is desirable. Waste that is processed in an anaerobic digestion facility is reduced to 40% of its original weight and significantly less

volume. Therefore, using anaerobic digestion decreases the volume of the landfill space required as well as associated methane emissions.

Academic

The leachate generated after it has been exhausted of its methane potential, is good for bamboo cultivation. Bamboo is used extensively in Ghana for constructional works to support structures as well as in the furniture industry. Therefore, it is recommended that further research involving cultivation of different plant species with leachate to determine the most suitable forest crop that can withstand the nutrient level of the leachate be undertaken.

It also recommended that research involving societal attitude and their readiness towards source separation of waste should be undertaken through social research. This research is advocated since the laboratory study indicates that source separated waste have high biogas potential compared to unsorted waste.

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11 APPENDICES

Appendix 1. Community garbage bin overflowing at Kaneshie, a suburb of Accra.

Appendix 2. Loaded hydrolysis reactors before digestion and digestate after digestion.

(a) H_{R1}

(b) (H_{R2})

Loaded hydrolytic reactors before digestion

(c) Waste after digestion.

Appendix 3. Dried digestate being sorted

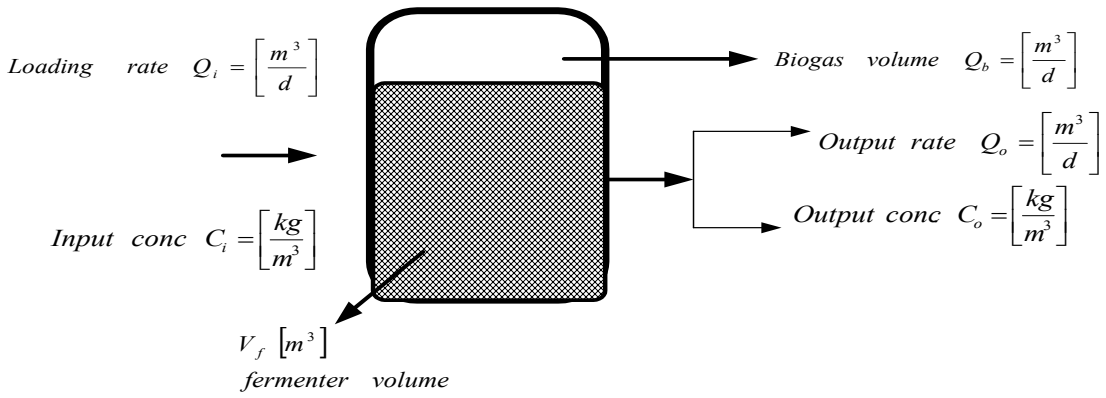
Appendix 4. Pictorial view of the components of the reactor set-up.

(a) The two parallel hydrolysis reactors (H_1 and H_2)

(b) The two insulated methane reactors (M_{R1} and M_{R2}),
gas clocks, stirrer and the heating device. The two blue tanks represents influent storage (right) and effluent left)

Appendix 5. Characteristics of the methane reactor.

Input and Output parameters



Process parameters

$$\text{Hydraulic Retention Time} \quad HRT = \frac{V_f}{Q_i} \quad [d]$$

$$\text{Volume load} \quad Lv = \frac{Q_i \bullet C_i}{V_f} = \frac{C_i}{HRT} \quad \left[\frac{kg}{m^3 \bullet d}\right]$$

Performane parameters

$$\text{Biogas yield} \quad y_b = \frac{Q_B}{Qi \bullet C_i} \quad \left[\frac{m^3}{kg}\right]$$

$$\text{Biogas rate } r_b = \frac{Q_B}{V_f} = Y_B \bullet L_v \quad \left[\frac{m^3}{m^3 \bullet d}\right]$$

$$\text{Specific biogas rate } r_s = \frac{Q_B}{V_f \bullet C_o} \quad \left[\frac{m^3}{kg \bullet d}\right]$$

Appendix 6. Buffer concentrations at ambient, 30 ^{o}C and 35 ^{o}C

Buffer concentrations at ambient temperature

Parameter	Influent mg/l					Effluent mg/l					% removal rate		
	Mean	S.D	Median	Min	Max	Mean	S.D	Median	Min	Max	Mean	S.D	Median
COD	3951	1719	3225	2190	6800	881	138	914	500	1000	74	11	74
BOD_5	760	14	760	750	770	80	42	80	50	110	89	6	89
OA	809	564	695	246	1912	37	2.	37	33	41	93	5	95
Cond	1.86	0.35	1.98	1.12	2.20	2.23	0.13	2.22	2.03	2.41			
Sal	0.79	0.17	0.9	0.50	1.0	1.0	0.08	1.0	0.9	1.10			
pH	7.79	0.23	7.81	7.39	8.07	7.79	0.05	7.99	7.92	8.11			
COD:BOD	4.30	0.08	4.35	4.3	4.40	11	6.10	12	7.2	16			
COD:OA	6.00	2.10	5.40	3.60	8.90	24	4	24.89	14	28			
COD:VOS	1.4	0.31	1.26	1.1	1.80								

Buffer concentration at 30 degrees

Parameter	Influent mg/l					Effluent mg/l					% removal rate		
	Mean	S.D	Median	Min	Max	Mean	S.D	Median	Min	Max	Mean	S.D	Median
COD	5139	2731	5925	1596	7800	616	9.9	636	355	710	83	12	90
BOD_5	1655	153	1632	1496	1860	36	21	33	15	65	99	1.1	98
OA	917	420	803	379	1504	68	9.0	68	53	78	91	4.2	92
Cond	1.8	0.20	1.8	1.42	2.01	2.12	0.08	2.11	2.01	2.3			
Sal	0.71	0.12	0.7	0.50	0.90	0.93	0.05	0.9	0.9	1.0			
pH	7.2	0.70	7.24	6.1	7.9	8.0	0.14	7..9	7.8	8.3			
COD:BOD	3.1	0.28	3.15	2.76	3.43	22.0	13.20	19	9.5	41			
COD:OA	5.5	2.02	5.21	2.84	9.27	9.15	1.59	9.0	6.72	12.9			
COD:VOS	3.41	2.01	3.70	1.41	6.37								

Buffer concentration at 35 degrees

Parameter	Influent mg/l					Effluent mg/l					% removal rate		
	Mean	S.D	Median	Min	Max	Mean	S.D	Median	Min	Max	Mean	S.D	Median
COD	3870	1484	3436	2275	6365	960	46	947	865	1000	73	9.0	73
BOD_5	1193	138	1193	1095	1290	87	10	87	80	94	93	2.0	93
OA	857	645	746	133	1835	18	2.0	18	15	20	96	4.0	97
Cond	2.26	0.15	2.27	2.05	2.45	2.68	0.22	2.59	2.41	2.99			
Sal	1.0	0.08	1.0	0.9	1.10	1.35	0.29	1.2	1.10	1.90			
pH	7.84	0.31	7.83	7.27	8.27	8.06	0.05	8.07	8.0	8.15			
COD:BOD	3.6	0.41	3.60	3.30	3.90	11.0	1.23	11.0	10.0	12			
COD:OA	5.31	4.7	5.31	3.4	17	53.42	4.0	53	48	59			
COD:VOS	1.50	0.49	1.52	0.06	2.28								

Appendix 7. Table of concentrations of the buffer liquid for the pretreated wastes.

(a) Mechanically sorted waste (8-40 mm)

Parameter	Influent mg/l					Effluent mg/l					% removal rate		
	Mean	S.D	Median	Min	Max	Mean	S.D	Median	Min	Max	Mean	S.D	Median
COD	10110	3510	10694	5100	15000	890	230	946	348	1165	90	5.0	92
BOD_5	4380	1508	4490	2850	5690	94	36	83	6	145	98	0.79	98
OA	3359	1160	3316	1699	4758	55	15	59	30	80	98	0.54	98
Cond	1.85	0.16	1.85	1.62	2.17	2.07	0.11	2.1	1.93	2.24			
Sal	0.8	0.11	0.8	0.6	1.0	0.86	0.09	0.86	0.7	1.0			
pH	7.0	0.28	7.1	6.62	7.4	7.9	0.08	7.87	7.79	8.02			
COD:BOD	2.65	0.94	2.52	1.85	3.7	10.37	3.22	10.85	6.1	3.65			
COD:OA	3.0	0.18	2.99	2.7	3.3	16	3.37	16.0	11.49	21.23			
COD:VOS	1.74	0.35	1.86	1.33	2.07								

(b) Market waste (source sorted)

Parameter	Influent mg/l					Effluent mg/l					% removal rate		
	Mean	S.D	Median	Min	Max	Mean	S.D	Median	Min	Max	Mean	S.D	Median
COD	6459	3342	5363	2790	10870	797	188	786	435	1090	85	6	87
BOD_5	2850	14	2850	2840	2860	57	32	57	34	80	98	1	98
OA	1517	952	1451	220	2914	58	10	54	48	78	93	6	
Cond	1.74	0.23	1.68	1.50	2.14	2.15	0.06	2.16	2.06	2.28			
Sal	0.68	0.12	0.65	0.50	0.90	0.93	0.05	0.9	0.9	1.0			
pH	7.35	0.60	7.45	6.20	8.26	7.73	0.09	7.76	7.56	7.86			
COD:BO													
D	3.73	0.02	3.74	3.72	3.75	16.72	9.51	16.72	9.99	23.44			
COD:OA	5.29	2.80	4.18	3.66	12.69	13.66	2.09	13.86	9.0	16.40			
COD:VO													
S	1.94	0.29	2.02	1.55	2.25								

(c) Manually sorted waste

Parameter	Influent mg/l					Effluent mg/l					% removal rate		
	Mean	S.D	Median	Min	Max	Mean	S.D	Median	Min	Max	Mean	S.D	Median
COD	10536	1882	11045	5655	12610	287	40.8	290	220	250	97	0.87	
BOD_5	4350	950	4350	3400	5300	144	2.5	144	142	147	97	0.7	
OA	2818	632	3021	1182	3243	65	16	70	42	84	98	0.57	
Cond	1.58	0.27	1.61	1.13	1.94	2.31	0.12	2.28	2.17	252			
Sal	0.58	0.14	0.6	0.3	0.8	0.98	0.09	1.00	0.8	1.10			
pH	5.87	0.34	5.80	5.55	6.78	7.68	0.18	7.65	7.41	7.99			
COD:BO													
D	2.32	0.52	2.24	1.84	2.87	1.99	0.03	2.0	1.96	2.02			
COD:OA	3.84	0.62	3.73	3.05	4.78	4.58	0.96	4.25	3.51	6.61			
COD:VO													
S	2.32	0.16	2.24	2.17	2.58								

(d) Shredded waste

Parameter	Influent mg/l					Effluent mg/l					% removal rate		
	Mean	S.D	Median	Min	Max	Mean	S.D	Median	Min	Max	Mean	S.D	Median
COD	8785	3378	9890	4249	12300	672	117	704	343	740	91	4	94
BOD_5	3860	408	3760	3360	4650	58	32	55	15	105	99	0.7	99
OA	1608	680	1521	642	2422	68	9.0	68	53	78	95	2.34	96
Cond	1.77	0.19	1.79	1.42	2.01	2.13	0.08	2.11	2.01	2.26			
Sal	0.71	0.12	0.7	0.50	0.90	0.94	0.05	0.9	0.9	1.0			
pH	7.16	0.70	7.24	6.11	7.94	7.97	0.14	7.92	7.81	8.25			
COD:BO													
D	2.30	0.23	2.34	1.89	2.61	16.69	12.0	12.0	6.0	44			
COD:OA	5.6	0.97	5.31	4.59	7.28	9.94	1.56	9.89	6.48	12.40			
COD:VO													
S	2.12	1.19	2.35	0.89	3.66								

(e) Ideal waste (control waste)

Parameter	Influent mg/l					Effluent mg/l					% removal rate		
	Mean	S.D	Median	Min	Max	Mean	S.D	Median	Min	Max	Mean	S.D	Median
COD	9816	2682	10228	6025	13120	212	39	222	108	240	98	0.17	98
BOD_5	6338	225	6335	6100	6580	72	270	75	35	100	99	0.46	99
OA	2616	877	2800	1320	3830	13	2.7	14	6.6	15	99	0.46	99
Cond	273	1.26	2.32	2.24	2.47	2.5	0.4	2.5	2.0	3.0			
Sal	1.33	1.01	1.0	1.0	1.2	1.34	0.14	1.4	1.1	1.5			
pH	6.85	0.87	7.04	5.3	7.91	8.2	0.1	8.12	8.02	8.32			
COD:BOD	1.6	0.10	1.60	1.50	1.60	3.4	1.7	2.8	2.1	6.0			
COD:OA	3.9	0.42	3.72	3.43	4.77	16.4	2.5	16	13.0	22			
COD:VOS	2.70	0.26	2.10	1.91	2.59								

(f) Simulated waste

Parameter	Influent mg/l					Effluent mg/l					% removal rate		
	Mean	S.D	Median	Min	Max	Mean	S.D	Median	Min	Max	Mean	S.D	Median
COD	5661	3203	4735	2095	9780	797	188	786	435	1090	82	9	84
BOD_5	2850	14	2850	2840	2860	72	11	72	65	80	97	0.40	97
OA	1459	944	1400	170	2845	58	10	54	48	78	92	8	96
Cond	1.75	0.22	1.7	1.5	2.14	2.15	0.1	2.2	0.9	1.0			
Sal	0.70	0.12	0.65	1.50	2.14	0.93	0.05	0.9	0.9	1.0			
pH	7.4	0.6	7.45	6.2	8.3	7.7	0.09	7.76	7.56	7.86			
COD:BOD	2.0	0.01	1.98	1.97	1.99	11.15	1.63	11.0	9.9	12.30			
COD:OA	4.85	2.7	3.8	3.29	12.29	13.7	2.09	13.8	9.0	16.4			
COD:VOS	3.1	1.1	3.3	1.7	4.2								

(g) Mechanical sorted (40-120) waste

Parameter	Influent mg/l					Effluent mg/l					% removal rate		
	Mean	S.D	Median	Min	Max	Mean	S.D	Median	Min	Max	Mean	S.D	Median
COD	5204	2016	5862	1597	7300	616	99	636	355	710	87	6	89
BOD_5	1481	109	1488	1344	1660	61	37	55	15	105	96	2.4	96
OA	952	403	900	380	1435	68	9	68	53	78	92	4	93
Cond	1.87	0.18	1.88	1.42	2.14	2.14	0.09	2.14	2.01	2.30			
Sal	0.78	0.11	0.80	0.50	0.90	0.95	0.05	0.95	0.9	1.00			
pH	7.27	0.52	7.30	6.11	7.94	7.92	0.11	7.89	7.78	8.25			
COD:BOD	2.7	0.20	2.7	2.43	3.0	15.4	13.01	11.0	5.84	40.5			
COD:OA	5.3	0.97	5.3	4.6	7.3	9.15	1.60	8.90	6.72	12.86			
COD:VOS	1.34	0.45	1.34	0.85	1.99								

Appendix 8. Poster of a published paper